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ANNUAL REPORT

Covering Period: July 1, 1990 - June 30, 1991

Submitted to the Office of the Science Advisor
U.S. Agency for International Development

"Reactive Diluents for High Solids Coatings
Based on Vernonia Oil"

Principal Investigator: Dr. Stoil Dirlikov
Grantee Institution: Eastern Michigan University

Collaborator: Dr. Peter Gitu
Institution: University of Nairobi

Collaborator: Mr. Patrick Muturi
Institution: Kenyan Industrial Research & Dev. Institute

Project Number: 9.035
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A.I.D. Grant Project Officer: Dr. Miloslav Rechcigl

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EXECUTIVE SUMMARY

The project objective is to establish a market for vernonia oil, a natural epoxidized vegetable oil produced in Africa by Vernonia galamensis. During the second year we have been able to reaffirm two very large multi-million dollar potential markets for vernonia oil as a reactive diluent for high solids alkyd and epoxy coatings (and air-pollution control) and for improvement of commercial epoxy resins.

Our results have been presented to the industrial and academic community and again highlighted in Chemical Engineering News and in Chemistry & Industry. Many chemical and coatings companies have expressed strong interest in our research. Hi-Tek Polymers has started a developmental trial and ten tons of vernonia seeds have been harvested.

In addition to exchange of scientific information between the three collaborating institutes: Coatings Research Institute (CRI) at Eastern Michigan University (EMU), Department of Chemistry of University of Nairobi (DC/UN), and Kenyan Industrial Research and Development Institute (KIRDI), Mr. Muturi (KIRDI) continues successfully his "vernonia" research in our CRI toward his Ph.D. degree. Mr. Muturi's stay at CRI has been extended for a second year. It allows his involvement in all major breakthroughs and discoveries, and later, when he returns back, transfer of "vernonia" technology to Kenya.

In summary, we have been able to fulfil our initial project goal to establish large markets for vernonia oil, which will drive the production of Vernonia galamensis in Africa, to transfer technology to Africa, and train African scientists.

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SECTION I

A. Research Objectives

A list and copies of the papers published, presentations, and patent disclosures submitted on our vernonia project are attached in Addendum I and III respectively.

The Ref. 18 was submitted for publication in March 1991 and represents an up-to-date progress report with research objectives and accomplishments.

B. Research Accomplishments

See Part A, Section I.

C. Scientific Impact of Collaboration

Scientific information has been exchanged among the three participants of the project: Coatings Research Institute (CRI) at Eastern Michigan University, Kenyan Industrial Research and Development Institute (KIRDI), and the Department of Chemistry at the University of Nairobi (DC/UN).

Mr. Patrick Muturi from KIRDI continues successfully his research at CRI on vernonia oil towards his Ph.D. degree with joint advisory committee: Dr. P. Gitu (DC/UN) and Dr. S. Dirlikov (CRI). His one year stay at CRI has been extended for a second year as a part of the collaboration and training plan program of the project. His research proceeds very well and we are very happy to have him at CRI. Mr. Muturi stay allows his involvement in all major breakthroughs and discoveries at CRI during the first year, and later, when he returns back - transfer of vernonia oil technology to Kenya.

D. Description of Project Impact

Our research has reaffirmed two large multi-million dollar markets for application of vernonia oil:

- as a reactive diluent in alkyd and epoxy coatings formulations, and
- for improvement (toughening, etc.) of commercial epoxy resins.

Our results have been presented to the industrial and academic community and again highlighted at the ACS Meeting, Washington, August 1990 in Chemical Engineering News, September 10, 1990, pp. 22 and Chemistry and Industry, No. 10, May 21, 1990, pp. 311. Many coatings and epoxy resins producers in USA, America, Europe, Asia and Africa have expressed strong interest in our research. Based on our results, Hi-Tek Polymers, Inc. (Rhone Poulenc USA Division) has started developmental trials on production of Vernonia galamensis, the plant which produces vernonia oil, and ten tons of vernonia seeds have been harvested.

E. Strengthening of Developing Country Institutions

See Part C, Section I.

F. Future Work

In summary, we have been able to fulfil our initial project goal to establish potential large markets for vernonia oil, which could drive the production of Vernonia galamensis in Africa, to transfer technology to Africa, and train African Scientists. We have demonstrated that vernonia oil is an attractive reactive diluent for high solids long, medium, and short oil alkyd coatings formulations and for improvement (toughness, etc.) of commercial epoxy resins. Vernonia oil does not need to be modified for these applications, as described in the initial plan/program. It is used directly without any modification. We, therefore, believe that these applications are industrially very attractive. No other revisions of the plan/program have been done or planned.

Goal of the third year is to complete our on-going research and write (and submit) several large papers in order to dissiminate our results in the coatings and polymer scientific and managerial communities. If time (and money) allows, we will explore several attractive new areas for potential applications of vernonia oil; the results of which may be useful for our next proposal to USAID.

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SECTION II

A. Managerial Issues

As mentioned in our first report, CRI has received three other grants in addition to that of U.S.A.I.D. on the development of high solids coatings on vernonia oil: South Coast Air Quality Management District ($196,000 for two years), State of Michigan ($40,000 for two years), and Paint Research Associates ($40,000 for two years). In addition to Mr. Muturi from KIRDI, we have been able to hire, during the second year, one post-doctoral fellow and one graduate student working on the project. This is one of the reasons why the initial three-year plan/program, as submitted to U.S.A.I.D., has been completed.

B. Budget

Budget issues have been handled by Project Director Dr. John Graham. The financial status report shows transactions of $14,354 only. The U.S.A.I.D. operating account has been "frozen" during the second year.

Research during the third year will be funded by all four accounts (see Section II.A).

C. Special Concerns

Two patent disclosures have been submitted to the Office of Research Development, EMU, and several others are in preparation on application of vernonia oil as a reactive diluent, toughening of epoxy resins, or fuel. See Addendum I and III, and Part D, Section II. Unfortunatley, EMU does not have enough funds to file our patent disclosures.

D. Collaboration, Travel, Training, and Publications

For collaborative activities, see Part C, Section I; For List of travel/training, see Addendum I; For list of papers published, see Addendum I.

List of Anticipated Activities

1. I. Frischinger, S. Dirlikov, Toughening of Epoxy Resins by Epoxidized Vegetable Oils, Poster Session, Gordon Research Conference on High Performance Thermosetting Polymeric Materials, Plymouth State College, Plymouth, NH, July 1991.

2. I. Frischinger, S. Dirlikov, Toughening of Epoxy Resins by Epoxidized Vegetable Oils, Poster Session, Gordon Research Conference on Chemistry and Physics of

Coatings and Film, Colby-Sawyer College (N), New London, NH, July/August 1991.

3. I. Frischinger, S. Dirlikov, Two-Phase Epoxy Interpenetrating Thermosets, The Fourth Chemical Congress of North America, New York, August 1991, PMSE 87, Polym. Mater. Sci. Eng. 1991, 65, 178-9.

4. I. Frischinger, S. Dirlikov, Two-Phase Epoxy Interpenetrating Thermosets, Chapter in "Interpenetrating Polymer Networks", Advances in Chemistry Series, Editors: L. Sperling, D. Kempner, L. Utracki, American Chemical Society (in preparation).

5. P. Muturi, D. Wang, S. Dirlikov, Partially Epoxidized Vegetable Oils as Reactive Diluents for High Solids Coatings, 19th Annual Waterborne, Higher-Solids, and Powder Coatings Symposium, New Orleans, LA, February 1992 (accepted).

6. P. Muturi, Il Frischinger, S. Dirlikov, Two-Phase Epoxy Coatings, Morphology and Properties, 203th ACS Meeting, PMSE Division, San Francisco, CA, April 1992 (in preparation).

7. P. Muturi, D. Wang, S. Dirlikov, Epoxidized Vegetable Oils as Reactive Diluents, I Comparison of Vernonia, Epoxidized Soybean, and Linseed Oils, J. Coatings Technology (in preparation).

8. P. Muturi, D. Wang, S. Dirlikov, Epoxidized Vegetable Oils as Reactive Diluents, II, Alkyd Resins, J. Coatings Technology (in preparation).

9. P. Muturi, I. Frischinger, S. Dirlikov, Epoxidized Vegetable Oils as Reactive Diluents, III, Epoxy Resins and Coatings, J. Coatings Technology (in preparation).

E. Request for A.I.D. or BOSTID Actions

We will welcome any help from AID/SCI or BOSTID staff.

ADDENDUM I

LIST OF PAPERS, PATENT DISCLOSURES, PRESENTATIONS, AND TRAVEL

The person involved is underlined.
Copies are attached in Addendum III.

1. S. Dirlikov (invited speaker), New Reactive Diluents for High Solids Coatings, Aqualon-Hercules Research Center, Wilmington, DE, August 1990.

2. S. Dirlikov (invited speaker), New Reactive Diluents for High Solids Coatings, Rohm & Haas Research Center, Spring House, PA, August 1990.

3. I. Frischinger, S. Dirlikov, Y. Feng and R. Pearson; Toughening of Epoxy and Propargyl Terminated Resins, 200th ACS Meeting, PMSE Division, Washington, D.C., August 1990, abstract PMSE 130.

4. S. Dirlikov, I. Frischinger and M. S. Islam; Application of Vegetable Oils in Polymer Chemistry, 200th ACS Meeting, CELL Division, Washington, D.C., August 1990, abstract: CELL 18.

5. M. S. Islam, X. Wu, T. J. Lepkowski, S. K. Dirlikov, New Reactive Diluents for High Solids Coatings, 200th ACS Meeting, Washington, D.C., August 1990, abstract PMSE 221.

6. S. Dirlikov, M.S. Islam, P. Muturi, Vernonia Oil: A New Reactive Diluent, Modern Paint and Coatings, 1990, 80 (8), 48-54.

7. S. Dirlikov (invited speaker), New Reactive Diluents for High Solids Coatings, Paint Research Associates, Detroit, MI, September 1990.

8. S. Dirlikov, M. S. Islam, I. Frischinger, T. Lepkowski, and P. Muturi, Vernonia Oil: A New Reactive Diluent for Alkyd and Epoxy Resins and Coatings, European Polymers Paint Colour Journal, 1990, 180 (4272), 666-687.

9. F. Jones and S. Dirlikov, Fuels Derived from Vegetable Oils and Animal Fats; Process for Production of Same, Eastern Michigan University Patent Disclosure, October 1990.

10. S. Dirlikov (invited speaker), Vernonia Oil: A New Reactive Diluent, Howard University, Washington, DC, October 1990.

11. S. Dirlikov (invited speaker), New Reactive Diluents for Reactive Coatings, First North American Research Conference on Organic Coatings: Science and Technology, Hilton Head, SC, December 1990.

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12. I. Frischinger, S. Dirlikov, Toughening of Epoxy Resins by Epoxidated Soybean Oil, Chapter in "Rubber-Toughened Plastics", Advances in Chemistry Series, Editors: C.K. Riew, A. Kinloch, American Chemical Society (submitted).

13. S. Dirlikov, M.S. Islam, Il Frischinger, T. Lepkowski, and P. Muturi, Vernonia Oil: A New Reactive Diluent for High Solids Alkyd and Epoxy Resins and Coatings, 18th Annual Waterborne, Higher-Solids, and Powder Coatings Symposium, New Orleans, LA, February 1991.

14. S. Dirlikov and I. Frischinger, Toughening of Epoxy Resins with Epoxidized Vegetable Oil, Eastern Michigan University patent disclosure, February 1991.

15. I Frischinger, S. Dirlikov, Toughening of Epoxy Resins by Epoxidized Vegetable Oils, POLYMER (in press).

16. S. Dirlikov, 1991 Midwest Industrial Uses Conference "Agricultrual Resources in Industry - Biotech Product and Business Opportunities for the 90s", Michigan Molecular Institute, East Lansing, MI, May 1991.

17. S. Dirlikov (invited speaker), I. Frischinger, M.S. Islam, L. Watkins, P. Muturi, T. Lepkowski, Low VOC Coatings Based on Vernonia Oil Reactive Diluents, International SAMPE Environmental Conference Series, "Environment in the 1990's - A Global Concern", 1991, 1, 79-22, San Diego, CA, May 1991.

18. S. Dirlikov (invited speaker), I. Frischinger, M.S. Islam, T. Lepkowski, P. Muturi, Vernonia Oil: A New Reactive Diluent for High Solids Alkyd and Epoxy Resins and Coatings, Engineering Society of Detroit and American Society of Manufacturers, Advanced Coatings Technology Conference, Dearborn, MI, June 1991, Conference Proceedings, 57-65.

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ADDENDUM II

FINANCIAL STATUS REPORT

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FINANCIAL STATUS REPORT

(Long Form)

(Follow instructions on the back)

1. Federal Agency and Organizational Element to Which Report is Submitted Agency For International Dvlpt.	2. Federal Grant or Other Identifying Number Assigned By Federal Agency DHR-5542-SS-9023-00	OMB Approval No. 0348-0039	Page 1 of 1 pages

3. Recipient Organization (Name and complete address, including ZIP code)
Eastern Michigan University
230 Business & Finance Bldg.
Ypsilanti, MI 48197

4. Employer Identification Number 38-6005-986-A-1	5. Recipient Account Number or Identifying Number 5-22138	6. Final Report ☐ Yes ☒ No	7. Basis ☐ Cash ☒ Accrual
8. Funding/Grant Period (See instructions) From: (Month, Day, Year) 6-9-89	To: (Month, Day, Year) 7-31-92	9. Period Covered by this Report From: (Month, Day, Year) 01-01-91	To: (Month, Day, Year) 06-30-91

10. Transactions:	I Previously Reported	II This Period	III Cumulative
a. Total outlays	117,511	14,354	131,865
b. Refunds, rebates, etc.	-	-	-
c. Program income used in accordance with the deduction alternative	-	-	-
d. Net outlays *(Line a, less the sum of lines b and c)*	117,511	14,354	131,865
Recipient's share of net outlays, consisting of: e. Third party (in-kind) contributions	-	-	-
f. Other Federal awards authorized to be used to match this award	-	-	-
g. Program income used in accordance with the matching or cost sharing alternative	-	-	-
h. All other recipient outlays not shown on lines e, f or g	-	-	-
i. Total recipient share of net outlays *(Sum of lines e, f, g and h)*	-	-	-
j. Federal share of net outlays (line d less line i)			131,865
k. Total unliquidated obligations			-0-
l. Recipient's share of unliquidated obligations			-0-
m. Federal share of unliquidated obligations			-0-
n. Total federal share (sum of lines j and m)			131,865
o. Total federal funds authorized for this funding period			150,000
p. Unobligated balance of federal funds *(Line o minus line n)*			18,135
Program income, consisting of: q. Disbursed program income shown on lines c and/or g above			-
r. Disbursed program income using the addition alternative			-
s. Undisbursed program income			-
t. Total program income realized *(Sum of lines q, r and s)*			-

11. Indirect Expense	a. Type of Rate *(Place "X" in appropriate box)* ☐ Provisional ☐ Predetermined ☐ Final ☐ Fixed			
	b. Rate 30% S.W.B.	c. Base 92,483	d. Total Amount 27,745	e. Federal Share 27,745

12. *Remarks. Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.*

*Questions should be directed to Melissa Hammonds (313) 487-0027

13. Certification: **I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.**

Typed or Printed Name and Title Susan Merrick, Controller	Telephone (Area code, number and extension) (313) 487-0027*
Signature of Authorized Certifying Official	Date Report Submitted

Previous Editions not Usable
NSN 7540-01-012-4285

269-103

Standard Form 269 (Rev. 4-88)
Prescribed by OMB Circular A-102

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FINANCIAL STATUS REPORT

(Long Form)

Please type or print legibly. The following general instructions explain how to use the form itself. You may need additional information to complete certain items correctly, or to decide whether a specific item is applicable to this award. Usually, such information will be found in the Federal agency's grant regulations or in the terms and conditions of the award (e.g., how to calculate the Federal share, the permissible uses of program income, the value of in-kind contributions, etc.). You may also contact the Federal agency directly.

Item	Entry
1, 2 and 3.	Self-explanatory.
4.	Enter the employer identification number assigned by the U.S. Internal Revenue Service.
5.	Space reserved for an account number or other identifying number assigned by the recipient.
6.	Check *yes* only if this is the last report for the period shown in item 8.
7.	Self-explanatory.
8.	Unless you have received other instructions from the awarding agency, enter the beginning and ending dates of the current funding period. If this is a multi-year program, the Federal agency might require cumulative reporting through consecutive funding periods. In that case, enter the beginning and ending dates of the grant period, and in the rest of these instructions, substitute the term "grant period" for "funding period."
9.	Self-explanatory.
10.	The purpose of columns, I, II and III is to show the effect of this reporting period's transactions on cumulative financial status. The amounts entered in column I will normally be the same as those in column III of the previous report *in the same funding period*. If this is the first or only report of the funding period, leave columns I and II blank. If you need to adjust amounts entered on previous reports, footnote the column I entry on this report and attach an explanation.
10a.	Enter total gross program outlays. Include disbursements of cash realized as program income if that income will also be shown on lines 10c or 10g. Do not include program income that will be shown on lines 10r or 10s. For reports prepared on a cash basis, outlays are the sum of actual cash disbursements for direct costs for goods and services, the amount of indirect expense charged, the value of in-kind contributions applied, and the amount of cash advances payments made to subrecipients. For reports prepared on an accrual basis, outlays are the sum of actual cash disbursements for direct charges for goods and services, the amount of indirect expense incurred, the value of in-kind contributions applied, and the net increase or decrease in the amounts owed by the recipient for goods and other property received, for services performed by employees, contractors, subgrantees and other payees, and other amounts becoming owed under programs for which no current services or performances are required, such as annuities, insurance claims, and other benefit payments.
10b.	Enter any receipts related to outlays reported on the form that are being treated as a reduction of expenditure rather than income, and were not already netted out of the amount shown as outlays on line 10a.
10c.	Enter the amount of program income that was used in accordance with the deduction alternative.
Note:	Program income used in accordance with other alternatives is entered on lines q, r, and s. Recipients reporting on a cash basis should enter the amount of cash income received; on an accrual basis, enter the program income earned. Program income may or may not have been included in an application budget and/or a budget on the award document. If actual income is from a different source or is significantly different in amount, attach an explanation or use the remarks section.
10d, e, f, g, h, i and j.	Self-explanatory.
10k.	Enter the total amount of unliquidated obligations, including unliquidated obligations to subgrantees and contractors. Unliquidated obligations on a cash basis are obligations incurred, but not yet paid. On an accrual basis, they are obligations incurred, but for which an outlay has not yet been recorded Do not include any amounts on line 10k that have been included on lines 10a and 10j. On the final report, line 10k must be zero.
10l.	Self-explanatory.
10m.	On the final report, line 10m must also be zero
10n,	o, p, q, r, s and t. Self-explanatory.
11a.	Self-explanatory.
11b.	Enter the indirect cost rate in effect during the reporting period.
11c.	Enter the amount of the base against which the rate was applied.
11d.	Enter the total amount of indirect costs charged during the report period.
11e.	Enter the Federal share of the amount in 11d
Note:	If more than one rate was in effect during the period shown in item 8, attach a schedule showing the bases against which the different rates were applied, the respective rates, the calendar periods they were in effect, amounts of indirect expense charged to the project, and the Federal share of indirect expense charged to the project to date.

ADDENDUM III

COPIES OF PAPERS, PATENT DISCLOSURES,
AND PRESENTATIONS
(Follow the list in Addendum I.)

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1. S. Dirlikov (invited speaker), New Reactive Diluents for High Solids Coatings, Aqualon-Hercules Research Center, Wilmington, DE, August 1990.

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2. S. Dirlikov (invited speaker), New Reactive Diluents for High Solids Coatings, Rohm & Haas Research Center, Spring House, PA, August 1990.

3. I. Frischinger, S. Dirlikov, Y. Feng and R. Pearson; Toughening of Epoxy and Propargyl Terminated Resins, 200th ACS Meeting, PMSE Division, Washington, D.C., August 1990, abstract PMSE 130.

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POLYMERIC MATERIALS SCIENCE and ENGINEERING

Proceedings of the ACS Division of Polymeric Materials: Science and Engineering

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TOUGHENING OF EPOXY AND PROPARGYL TERMINATED RESINS

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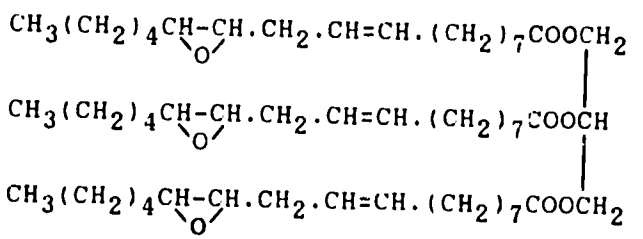
The toughening of two thermosetting materials, epoxy resins and propargyl terminated resins (PTR), has been described in this paper.

MODIFICATION OF EPOXY RESINS

It is known that a small amount of discrete rubbery particles with an average size of several microns, randomly distributed in a glassy, brittle epoxy resin, dissipates part of the impact energy thus improving crack and impact resistance without deterioration of other properties of the initial epoxy resins.

The epoxy resin toughness is usually achieved by separation of a rubbery phase with a unimodal size distribution from the matrix during the curing process. Different carboxy- or amino-terminated oligomers are used for the formation of the rubbery phase. Some of these oligomers are quite expensive. However, epoxidized vegetable oils open new possibilities. The epoxy resins based on epoxidized vegetable oils and commercial amines are elastomers at room temperature. They have low glass transition temperatures, in the range of -80°C to 0°C, which depends on the nature of the epoxidized oil and that of the diamine used for their B-staging. They are very suitable for toughening of commercial epoxies. Two types of epoxidized vegetable oils have been used in the present studies for epoxy toughening: vernonia oil and epoxidized soybean oil (ESO).

Vernonia oil, a naturally occurring epoxidized vegetable oil, contains predominantly (~80%) trivernolin, a triglyceride of vernolic acid:



Vernonia galamensis, the source of vernonia oil, is a new potential oil seed crop in Africa, Asia and Central America. It is at a developmental stage in several African countries, especially in Zimbabwe and Kenya; and has a potential to soon become an industrial crop. Several major chemical and coatings companies have expressed strong interest in cultivation of Vernonia galamensis and vernonia oil production.

Our initial attempts for toughening of epoxy resins have been carried out directly with vernonia oil. For this purpose, homogeneous mixtures of commercial epoxy resin (EPON 825) and commercial amines (DDS, DAPM, isophorone diamine, different aliphatic di- and polyamines, etc.), containing 10 to 25 percent vernonia oil have been cured according to a "standard" curing procedure for epoxy resin. The commercial epoxy resins have higher reactivity with commercial diamines than the epoxy groups of vernonia oil. As a result, they form a rigid matrix at 70°C in which vernonia oil separates as liquid phase droplets. The

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electromicrograph of a formulation based on EPON 825, isophorone diamine and vernonia oil shows a rigid matrix with homogeneous distribution of vernonia droplets with diameter in the range of 1 micron (Figure 1). Unfortunately, these droplets do not cure at a high temperature of 150°C with the excess of diamine. Instead, plastification occurs resulting in lower glass transition temperature of the rigid matrix observed in DSC.

We have been able to obtain a two-phase system with rubbery vernonia particles by using vernonia B-staged materials instead of pure vernonia oil as described in the experimental section. Vernonia particles again separate from the initial homogeneous mixture of epoxy resin, diamine and vernonia B-staged material during curing. In this procedure, however, the final thermoset consists of a rigid epoxy matrix with randomly distributed small rubbery "vernonia" spherical particles (Figure 2). Diamine molecules on the interface are expected to react with both the epoxy groups of the commercial epoxy resin and the unreacted epoxy groups of vernonia oil, and will presumably form a chemical bonding between the rigid matrix and the rubbery particles.

Plastification phenomena of higher temperature (150°C) described above for pure vernonia oil has been observed here for vernonia B-staged materials as well, if the solubility parameters of the epoxy matrix and vernonia rubber phase are similar. Such formulations are based on less polar diamines; for example, the mixture of epoxy resin, DAPM, and vernonia B-staged material. The plastification in this case has been avoided by a two-step curing procedure (see the experimental section). The general rule is to carry out the epoxy resin cure at a lower temperature and build the rigid matrix, then to increase the temperature and cure the less reactive vernonia oil with the excess of diamine into rubbery particles and simultaneously post-cure the matrix.

Plastification phenomena, however, is not observed for formulations based on more polar diamines (than DAPM), for instance, DDS. In this case, the solubility parameters of the "polar" epoxy matrix and "non-polar" vernonia phase are quite different. DDS based formulations, therefore, do not require a two-step curing procedure in order to build the molecular weight of the matrix at lower temperature. They form two-phase thermosets directly at 150°C (see experimental section).

The particle diameter is a function of the incompatibility of vernonia B-staged material and the epoxy matrix. We have been able to vary the particle diameter in the range of the desirable particle size for toughening thermosets, e.g. of 5 to 50 microns. In general, larger particles and even macroscopic total phase separation are obtained for less compatible systems with more polar diamine, for instance, DDS for curing of the rigid matrix.

The epoxy thermoset based on EPON 825, DAPM, and vernonia/dodecaneamine B-staged material shown on the electromicrograph, has broad rubbery vernonia oil particles distribution in the range of 5 to 35 microns diameter (Figure 2).

Typical DMA is shown on Figure 3. Glass transition temperatures of the vernonia rubbery phase and the rigid epoxy matrix EPON 825 are - 22° and 160°C, respectively. DAPM is used as diamine curing agent for the matrix, whereas dodecanediamine is used for vernonia oil B-staging. The glass transition of the matrix corresponds to the glass transition temperatures of a pure epoxy resin castings (160°C). We believe there is no extensive internal plastification.

Similar results have been obtained with ESO. Surprisingly, ESO rubbery particles have smaller size in the range of 0.1 to 10 microns and much lower glass transition temperature (-70°C) than that based on vernonia oil.

Our initial results show improved fracture toughness (K_{IC}) for thus modified epoxy resins. Since epoxidized vegetable oils are practically resistant to water, the resulting two phase

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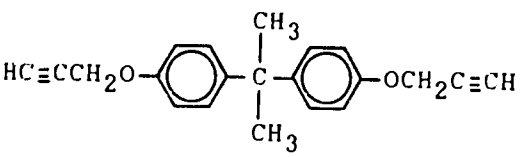
epoxy resins are expected to have lower water absorption. Also, the introduction of epoxidized vegetable oils into the commercial epoxy resin will result in price reduction.

MODIFICATION OF PROPARGYL TERMINATE RESINS

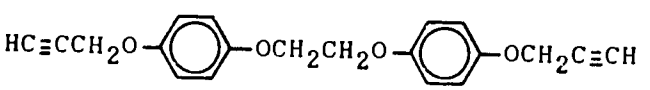
PTR monomers are available in pure state in one-step, easy preparation in quantitative yield from industrially produced inexpensive starting raw materials (2). The procedure is suitable for industrial production in large scale and the monomers are potentially available at a low price. PTR have a set of properties including physico-mechanical and dielectric properties which are superior to that of other thermosetting materials. They appear to be a very attractive low cost substitute for the expensive acetylene terminated resins and are a potential substitute for the hydrophilic epoxy resin and bismaleimides as a hydrophobic matrix in advanced composites, electronics, adhesives, and coatings.

Dipropargyl ether of bisphenol A (DPEBA) appears to be the most attactive monomer:



The main disadvantage of the PTR based on DPEBA is their relatively low toughness: Fracture toughness, K_{Ic} is 387 (25°C), 401 (100°C), and 347 psi. $in^{0.5}$ (177°C).

In order to improve PTR toughess, we have prepared thermosets of dipropargyl ether of 3,3'-(ethylenedioxy)diphenol which has flexible ethyleneoxide central block:



Monomer and thermoset preparation and characterization will be discussed in the present paper.

EXPERIMENTAL

Vernonia oil has been kindly supplied by Dr. K. Carlson from the U.S.D.A. ESO is a Union Carbide product.

Two-phase epoxy thermosets have been prepared as follows: Vernonia oil was initially B-staged with amines. For this purpose a mixture of 100 g of vernonia oil and 25.63 g of 4,4'-methylenedianiline (DAPM) have been heated at 180°C for 40 hours under nitrogen. Similar results have been observed for vernonia B-staged material obtained from 25.9 g of 1,12-dodecanediamine and 100 g of vernonia oil heated at 180°C for 37 hours. The vernonia B-staged material based on DAPM or 1,12-dodecanediamine is added in 10, 20 or 30 weight percent to a stoichiometric mixture of diglycidyl ether of bisphenol A (Shell epoxy resin EPON 825) and DAPM or 4-aminophenyl sulfone (DDS). The resulting homogeneous formulation based on DAPM is additionally B-staged at 75°C for 95 minutes under nitrogen, and then poured into the casting mold and vacuumed. Final cure and post-cure are carried out at 75°C for 4 hours and 150°C for two hours respectively. The corresponding DDS formulation is B-staged at 150°C for 1 hour under nitrogen and then cured in the mold at 150°C for 2 hours. Both (DAPM or DDS) formulations produce excellent large castings.

Two-phase ESO/epoxy thermosets have been prepared in a similar manner.

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Electromicrographs have been taken by an Amray Electron Microscope, Model 1000B, whereas glass transition temperatures have been determined by DuPont Thermal Analyst 2100 instrument, DMA model 983 and DSC model 2910.

Dipropargyl ether of 3,3'-(ethylenedioxy)diphenol has been prepared, B-staged, and cured according to procedures typical for PTR (2).

CONCLUSION

Commercial epoxy resins have been toughened with epoxidized vegetable oils following a standard procedure for curing. The final thermoset has better toughness, lower water absorption, and potentially lower price. PTR, with a flexible central block, has been prepared and characterized for toughness.

ACKNOWLEDGMENT

We would like gratefully to acknowledge the financial support by the South Coast Air Quality District Management, U.S. Agency for International Development, the Paint Research Associates, and Michigan State.

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1. S. Dirlikov, I. Frischinger, M.S. Islam and J. Graham, Proc. of ACS Div. Polym. Mater.: Sci. and Eng., 62, 217 (1990).
2. S. Dirlikov, Proc. of ACS Div. of Polym. Mater.: Sci. and Eng., 62, 603 (1990).

FIGURE 1. ELECTROMICROGRAPH OF TWO-PHASE EPOXY RESIN: MATRIX BASED ON EPON 825 AND ISOPHORONE DIAMINE AND LIQUID PHASE OF VERNONIA OIL (20%).

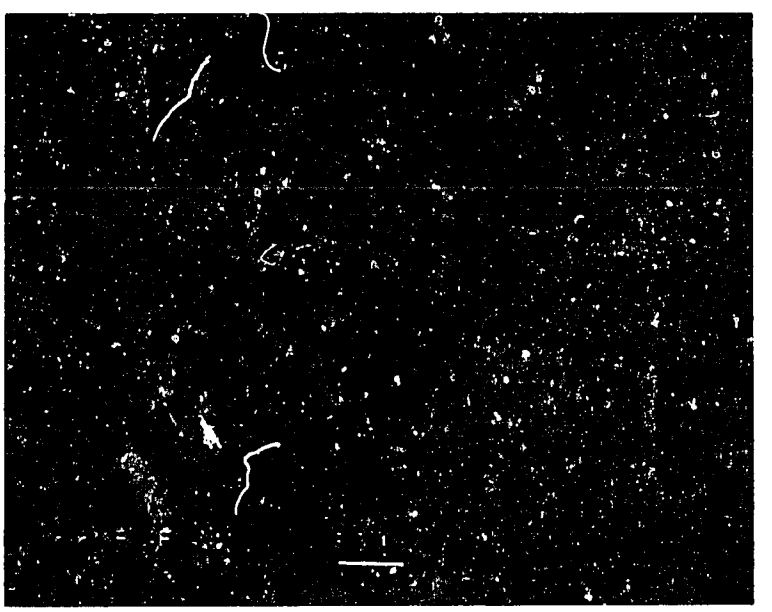

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FIGURE 2. ELECTROMICROGRAPH OF TWO-PHASE EPOXY RESIN BASED ON EPON 825, DAPM, AND 20% VERNONIA/DODECANEDIAMINE B-STAGED MATERIAL.

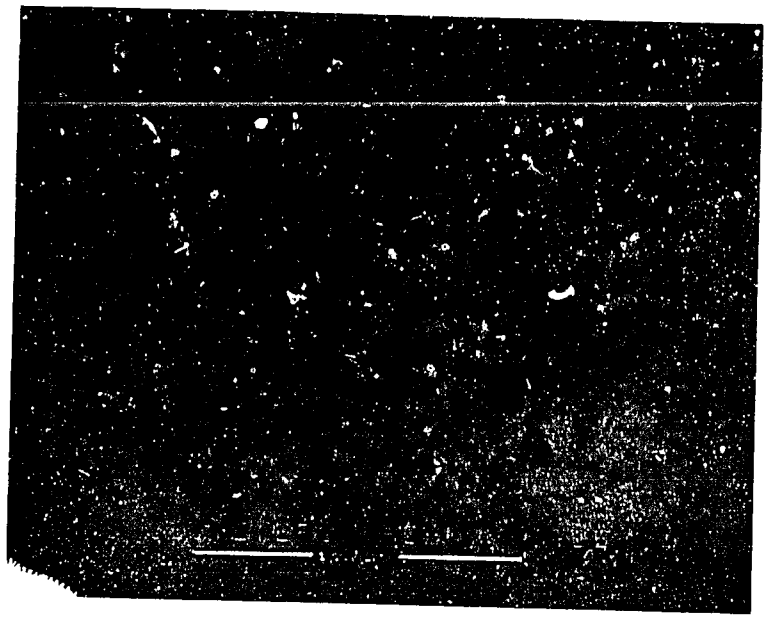
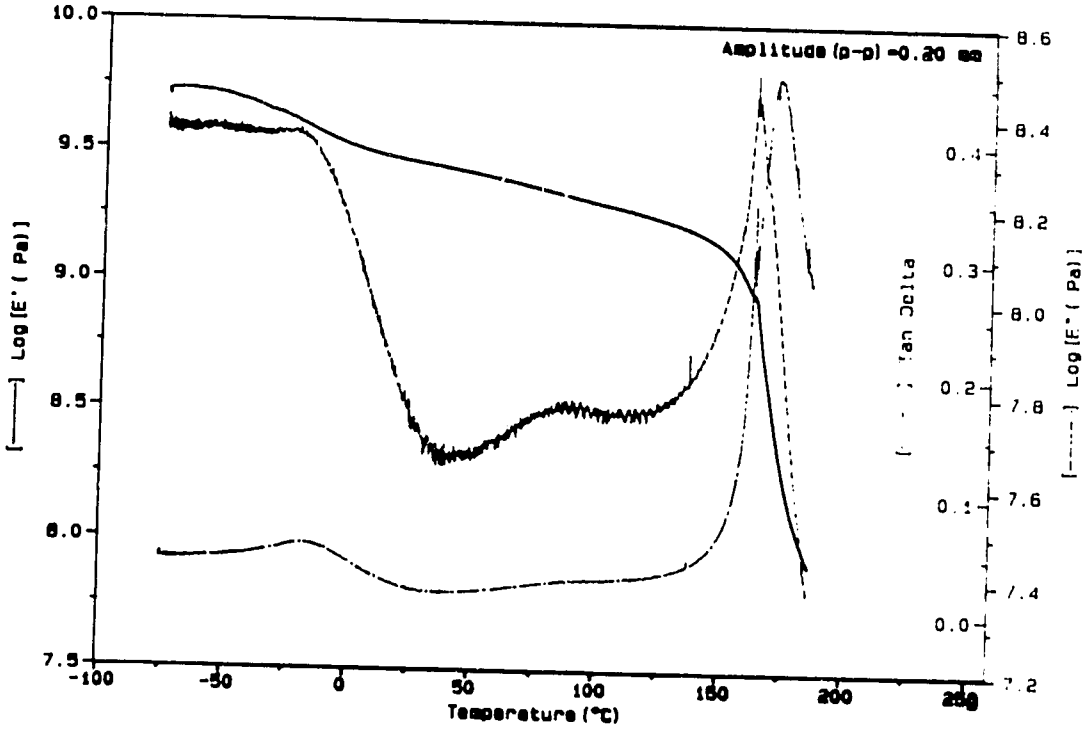


FIGURE 3. DMA OF TWO-PHASE EPOXY RESIN: MATRIX BASED ON EPON 825 AND DAPM (Tg = 160°C) AND RUBBERY PARTICLES (20%) OF VERNONIA OIL AND DODECANEDIAMINE (Tg = -22°C)



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4. S. Dirlikov, I. Frischinger and M. S. Islam; Application of Vegetable Oils in Polymer Chemistry, 200th ACS Meeting, CELL Division, Washington, D.C., August 1990, abstract: CELL 18.

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(To be filled in by Division)

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M. Safiqul Islam

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APPLICATION OF VEGETABLE OILS IN POLYMER CHEMISTRY, Stoil K. Dirlikov, Isabelle Frischinger, and M. Safiqul Islam, Coatings Research Institute, Eastern Michigan University, 430 W. Forest Avenue, Ypsilanti, MI 48197

The application of vegetable oils in polymer chemistry has been reviewed. In addition, authors' research on utilization of epoxidized vegetable oils has been summarized. Vernonia oil, a natural epoxidized vegetable oil, is at a development stage in several countries and appears to be a very attractive raw material for several large volume industrial applications. It is characterized by very low viscosity (in comparison to other epoxidized vegetable oils) and has a potential as a reactive diluent for high solid alkyd and epoxy coatings by replacing conventional solvents. Epoxy resins based on vernonia oil have low glass transition temperatures (-70°C) and are able to simultaneously improve the two major disadvantages of the commercial epoxy resins: low toughness and high water absorption. Finally, vernonia oil is a stabilizer and plasticizer of poly(vinyl chloride). In conclusion, vegetable oils appear to be a very attractive renewable resource for preparation of a broad variety of unique monomers and polymers.

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5. M. S. Islam, X. Wu, T. J. Lepkowski, S. K. Dirlikov, New Reactive Diluents for High Solids Coatings, 200th ACS Meeting, Washington, D.C., August 1990, abstract PMSE 221.

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NEW REACTIVE DILUENTS FOR HIGH SOLIDS COATINGS

Stoil K. Dirlikov, M. Safiqul Islam, Xiaosong Wu and T. J. Lepkowski*, Coatings Research Institute, Eastern Michigan University and *Paint Research Associates, 430 W. Forest Avenue, Ypsilanti, MI 48197

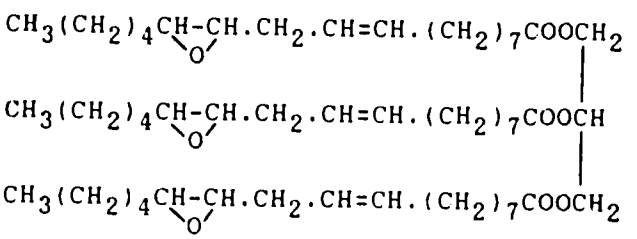
There is a strong need for reactive diluents in the reduction of non-reactive solvents in coating formulations. Recently, further and stricter measurers have been taken for air pollution control. In 1988, the U.S. Environmental Protection Agency announced a ban on construction of major air-polluting plants in Los Angeles and other U.S. cities in order to reduce air pollution, and in the same year the South Coast Air Quality District Management announced a plan for reduction of hydrocarbon emission in Orange County, California by 80 to 90 per cent over next five years. This plan requires reduction of volatile organic compound (VOC) emission from paints and varnishes from the current 22.1 tons per day to 2.9 tons per day several years from now. It is an impossible task with today's coatings technology. An attractive approach for air-pollution control is replacement of conventional solvents which produce VOC emission with reactive diluents.

This paper describes our initial evaluation of two new types of reactive diluents: vernonia oil and acetylene compounds for high solids alkyd and epoxy coating formulations.

VERNONIA REACTIVE DILUENTS

Vernonia galamensis, the source of vernonia oil, is a new potential oil seed crop in Africa, Asia, Central America and the Southwest U.S.A.. It is at a developmental stage in several African countries, especially in Zimbabwe and Kenya; and has a potential to soon become an industrial crop. Several major chemical and coatings companies have expressed strong interest in cultivation of *Vernonia galamensis* and vernonia oil production.

Properties of Vernonia Oil. Vernonia oil contains predominantly (~80%) trivernolin, a triglyceride of vernolic acid. Vernonia oil is a naturally occurring epoxidized vegetable oil containing one epoxy ring and one carbon-carbon double bond per each vernolic acid residue:



Vernonia oil has several unique features:

a. It is a transparent homogeneous liquid at room temperature with excellent solubility in many organic solvents, diluents, and paints.

b. Vernonia oil has a low viscosity of 300 cps at 50°F and 100 cps at 85°F.

c. It has a low melting point of ~36°F.

d. Vernonia oil has a homogeneous molecular structure consisting predominantly of identical triglyceride molecules which have three equal vernolic acid residues. In contrast, all other vegetable oils consist of a heterogeneous mixture of triglycerides with different fatty acid residues.

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e. It is expected to be available at a low price of approximately 45 to 75 cents per pound.
f. Toxicity of vernonia oil is expected to correspond to that of the epoxidized soybean and linseed oils which are industrially produced.

Vernonia vs. Other Epoxidized Vegetable Oils. We believe that vernonia oil does not compete with other epoxidized vegetable oils, i.e. epoxidized soybean oil and epoxidized linseed oil, which are industrially produced by epoxidation of unsaturated vegetable oils and have structures similar to vernonia oil. Epoxidized soybean and linseed oils are not suitable for coatings applications as reactive diluents based on their higher viscosity (in the range of 1000-2000 cps at 50°F), or at least they are less suitable than vernonia oil.

Vernonia Coatings. Ken Carlson and co-workers (1), from the U.S. Department of Agriculture have reported that "vernonia" coatings can be obtained directly from vernonia oil by a standard baking procedure at 150°C for 30 minutes in the presence of different drier systems. Our initial results have been published in Reference 2. The goal of our present study is determination of the drying mechanism and compatibility of vernonia oil with alkyd and other resins, characterization of these "vernonia" coatings, evaluation of different drier systems, and eventually improvement of their properties.

Drying Mechanism. We were interested in the drying mechanism of vernonia oil since it has two functionalities: unsaturated double bond and epoxy ring. For this purpose, we have compared the drying characteristics of triolein, vernonia oil, and epoxidized soybean oil in the presence of 0.5 per cent cobalt drier under baking conditions at 150°C for one hour. Epoxidized soybean oil does not form coatings at 185°C for several hours. Obviously, its epoxy groups do not polymerize under these conditions. Both triolein and vernonia oil form good coatings. These results show that vernonia oil drying is based on its unsaturated carbon-carbon double bonds and not on its epoxy functionality. This allows its application as a reactive diluent, not only in epoxy and epoxy-ester formulations, but in alkyd resins as well. Results also show that vernonia oil dries at lower temperature and much faster than the triolein. Good coatings have been obtained from vernonia oil at 150°C for half an hour. Triolein does not form coatings at 150°C for 1 hour. It forms coatings only at 180°C for 1.5 hours. The epoxy rings of vernonia oil probably activates the oxidation of the methylene group between the epoxy ring and the carbon-carbon double bond and we, therefore observe its faster drying in comparison to triolein.

Compatibility with Alkyd Resins. Compatibility studies have been carried out with Reichhold Beckosol long oil alkyds 10-560 and 10-060, medium oil alkyd 11-035, and short oil alkyd 12-005. Vernonia oil is compatible with all three types of alkyd resins at any ratio.

Drier Evaluation. We evaluated different driers and drier combinations for vernonia oil and for its 20% mixtures in alkyd resins. Cobalt drier at 0.1 per cent concentration form good coatings at 150°C for 1 hr. Zirconium drier even at higher concentration (0.5%) does not form coatings at higher temperature (160°C) and longer time (2 hours). Calcium and manganese driers have intermediate activity, weaker than the cobalt drier but stronger than the zirconium. Without going into further detail, Manchem manosec CD-44 drier gives the best results. It

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is more active than all other driers and drier combinations. It contains cobalt (0.6%), calcium (0.2%), and lithium (0.03%) carboxylates in mineral spirits.

Vernonia oil does not air dry with none of the driers at room temperature in several hours. It does dry slowly in about a week. However, alkyd resin mixtures containing 10 to 40% vernonia oil air-dry at room temperature within several hours.

Clear Coatings. We have compared the properties of the 2 mil thick coatings obtained under baking conditions in the presence of 0.04 per cent cobalt naphthenate drier at 150°C for one hour on cold rolled steel panels from vernonia oil, pure 10-560 and 10-060 long oil alkyds, and their mixture containing 20 per cent vernonia oil.

All coatings have good adhesion of 4B. Hardness is also good. Pencil hardness is H and Rocker Sward hardness is 12. Both adhesion and hardness improves at higher baking temperature and longer time. Flexibility, according to a standard test by bending the steel panel around 180°, is excellent. We did not observe any cracks or tape-off under microscope. The impact strength is also excellent. The direct impact strength is 150 pounds.inch., whereas the reverse is 140 pounds.inch.

All three types of coatings have the same properties which indicates that introduction of vernonia oil does not deteriorate the basic properties of alkyd resin.

Alkyd Paint Formulations. We also prepared a typical paint formulation shown on Table 1 and compared it to the paint formulations in which the initial long oil alkyd has been substituted with 20 and 40 per cent vernonia oil.

Table 2 compares the Brockfield viscosity, RCI drying times in hours at room temperature of coatings with 3 mil thickness, and volatile organic compound or VOC in lb. per gallon. The first paint formulation corresponds to the initial formulation based only on alkyd resin (Table 1). In the second paint formulation, 20% of the alkyd has been substituted with vernonia oil. Lower viscosity is observed for this formulation. Then, the next two formulations contain still 20% vernonia oil but their solvent content has been gradually reduced. The goal is to decrease the solvent to the point at which the viscosity of the paint formulation corresponds to the viscosity of the initial paint formulation without vernonia oil. These two formulations have much lower volatiles. The fifth paint formulation is exactly as the first one with the only difference being that it contains "our" new, more active CD-44 drier. Drying time of the paint formulations or tack-free time changes very little in the presence of vernonia oil, but sharply decreases in the presence of CD-44. Finally, the last formulation contains the new drier system and 20% of its alkyd resin has been substituted with vernonia oil. The important result here is that by introducing 20% vernonia oil in this formulation we are able to decrease the volatiles, and thus eventually reduce air-pollution, reduce the drying time, and maintain equal or lower viscosity than the initial paint formulation.

A potential problem for direct application of vernonia oil in alkyd formulations is an anticipated reaction between its epoxy groups and the terminal carboxyl groups of the alkyd resins. Our results show that vernonia oil does not change the can stability of the formulations. Obviously, the epoxy groups of vernonia oil have low reactivity and do not react with the free carboxyl groups of the alkyd resins under test conditions for can stability. The low reactivity of the epoxy groups of vernonia oil has been confirmed by additional experiments.

Q-UV test, which is decrease in gloss at 20° and 60° after exposure at UV light and humidity for a week, indicates that vernonia oil improves the coatings weatherability.

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Epoxy Coatings. Vernonia oil contains reactive epoxy groups and is an attractive reactive diluent for epoxy or epoxy ester formulations as well.

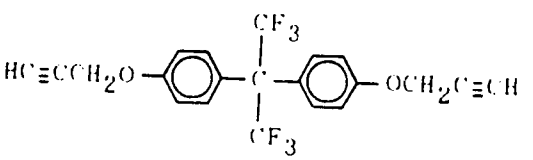
ACETYLENE REACTIVE DILUENTS

Different organic compounds with carbon-carbon triple bonds have been evaluated as reactive diluents for alkyd resins:

$CH{\equiv}C(CH_2)_8C{\equiv}CH$	I
$CH_3(CH_2)_3OCH_2C{\equiv}CH$	II
$CH_3OCH_2C{\equiv}CH$	III
$C_{13}H_{18}$ (1,7-cyclotridecadiyne)	IV
$CH_3C{\equiv}C(CH_2)_6C{\equiv}CCH_3$	V
$CH_3CH_2C{\equiv}C(CH_2)_4C{\equiv}CCH_2CH_3$	VI
$CH_3(CH_2)_2C{\equiv}C{-}C{\equiv}C(CH_2)_2CH_3$	VII
$CH_3(CH_2)_3C{\equiv}C.C(CH_3){=}CH_2$	VIII
$CH_3(CH_2)_3C{\equiv}CCH_2C{=}CH_2$	IX
$CH_3(CH_2)_4C{\equiv}C.C_6H_5$	X

Their selection includes different acetylene groups: terminal (I), aliphatic propargyl (II and III), isolated non-terminal (IV, V, and VI), conjugated with a second triple bond (VII) or carbon-carbon double bond (VIII), separated from a double bond by a methylene group (IX) and adjacent to a benzene ring (X). We observed rapid air-dry at room temperature of II, III, VII, VIII, and IX in several hours to several days in the presence of cobalt napthenate or of Manchem CD-44 drier.

Propargyl aromatic ethers are especially attractive as reactive diluents. Their preparation and characterization has been reviewed in Reference 3. Dipropargyl ether of hexafluorobisphenol A (DPBPA-F_6):



which is liquid, air-dries by itself at room temperature for two days in the presence of cobalt naphthenate. Alkyd resins containing 20% DPBPA-F_6 air dries under the same conditions for less than one hour and forms good coatings. Dipropargyl ether of resorcinol has similar drying characteristics. The properties of this type of coatings are under evaluation.

CONCLUSION

In summary, vernonia oil and acetylenic compounds are attractive reactive diluents for preparation of high solids alkyds and epoxy coating formulations with low VOC.

ACKNOWLEDGMENT

We would like gratefully to acknowledge the financial support by the South Coast Air Quality District Management, U.S. Agency for International Development, the Paint Research Asso-

ciates, and Michigan State. We would like to also thank Dr. John C. Graham, Coatings Research Institute and Dr. Robert Perdue from the U.S.D.A. for advice and many fruitful discussions.

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3. S.K. Dirlikov, Proceedings of ACS Div. of Polymeric Materials: Sci. and Eng., 62, 603 (1990).

TABLE 1. COMPOSITION OF PAINT FORMULATIONS IN WEIGHT PARTS

10-060 L.O. ALKYD	78.60
ODORLESS MINERAL SPIRITS	23.59
BYK BYKUMEN	3.77
NOUDEX NUXTRA CALCIUM 10% (PREMIX ABOVE)	1.12
DUPONT R-900 TiO2	150.97
T & W ATOMITE	37.74
NL CHEMICAL SD-1 BENTONE (ADD SLOWLY TO COWLS)	2.72
10-060 L.O. ALKYD	81.62
VERNONIA OIL (ADD TO GRIND)	
NUODEX NUXTRA COBALT 12%	0.46
NUODEX NUXTRA ZIRCO 24%	2.34
ODORLESS MINERAL SPIRITS	93.10
NUODEX EXKIN #2 (PREMIX THEN ADD)	1.62

TABLE 2. CHARACTERIZATION OF PAINT FORMULATION

	PAINT FORMULATION	BROOKFIELD VISCOSITY CPS	RCI DRYING TIME, HR	VOC LB./GAL.
1.	INITIAL 10-060	2640	13	3.15
2.	V.O. 20%	586	11	3.11
3.	V.O. 20% LESS SOLVENT	2260	15	2.63
4.	V.O. 20% LESS SOLVENT	3476	12	2.52
5.	INITIAL 10-060 DRIER CD-44	3344	3-4	2.50
6.	DRIER CD-44 V.O. 20%	780	4	2.60

6. S. Dirlikov, M.S. Islam, P. Muturi, Vernonia Oil: A New Reactive Diluent, Modern Paint and Coatings, 1990, 80 (8), 48-54.

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Modern Paint and Coatings

Formerly PAINT AND VARNISH PRODUCTION

AUGUST 1990 **VOL. 80, NO. 8**

FEATURES

Raw Materials Outlook: New Capacity Eases Shortages 40

Added production capacity and a cooling economy have combined to alleviate several raw material shortages. Our annual overview analyzes trends in the supply and demand of raw materials in the paint and coatings industry.

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By Stoil Dirlikov, M. Safiqul Islam and Patrick Muturi

Vernonia oil shows promise as a reactive diluent for high-solids alkyds and epoxy coating formulations. It has low viscosity, a low melting point and can be inexpensively produced.

Metallic Flake Pigments: Brilliant Additions To Paint 56

By Lise B. Carey

New improvements and applications for metallic pigments in coatings have led to increased demand for aluminum and copper pastes and powders.

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ON THE COVER:

This month's cover photo depicts mixed metal oxide pigment manufactured by Drakenfeld Colors, Washington, Pa. (Photo courtesy of Ciba-Geigy Corp.)

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BPA

Vernonia Oil: A New Reactive Diluent

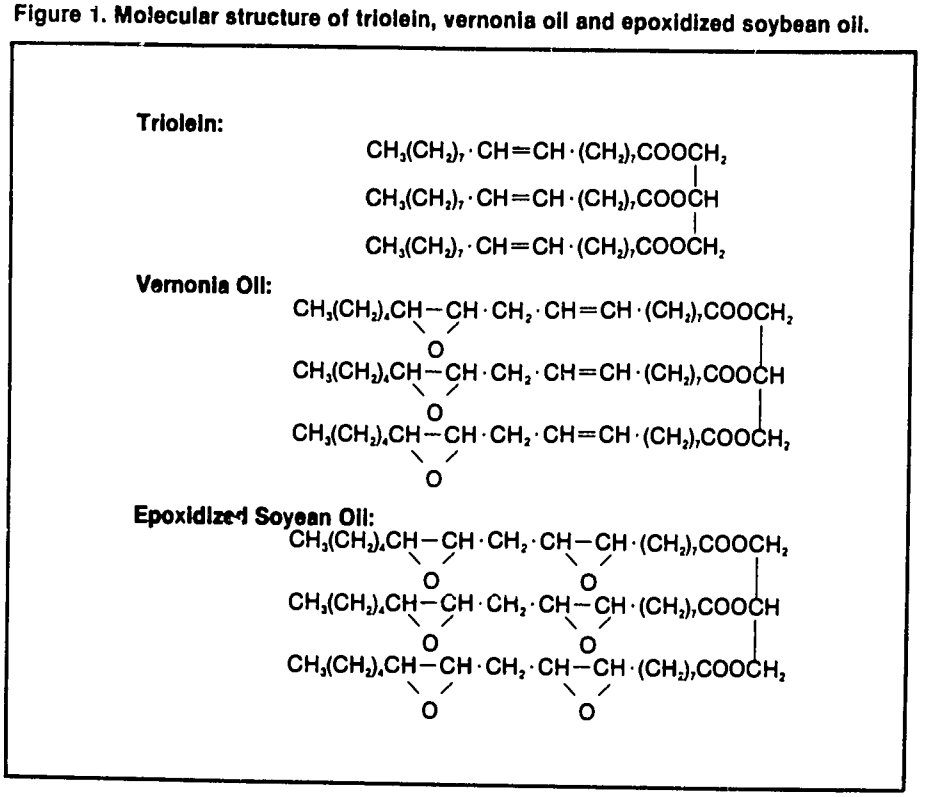
By **Stoil Dirlikov** and **M. Safiqul Islam,**
Coatings Research Institute, Eastern Michigan University,
and **Patrick Muturi,**
Kenyan Industrial Research and Development Institute

THERE IS A NEED for reactive diluents in the reduction of non-reactive solvents in coating formulations for air pollution control. Recently, more restrictive measures have been taken for reduction of air pollution. In 1988, the U.S. Environmental Protection Agency (EPA) announced a ban on construction of major air-polluting plants in Los Angeles and other cities, and in the same year the South Coast Air Quality District Management announced a plan for reduction of hydrocarbon emissions in Orange County, Calif., by 80 to 90 percent over the next five years. This plan requires reduction of volatile organic compound (VOC) emissions from paints and varnishes from the current 22.1 tons per day to 2.9 tons per day several years from now. It is an impossible task with today's coatings technology.

The objective of our research is the application of vernonia oil as a reactive diluent for high-solids alkyd, epoxy, and epoxy-ester coating formulations by replacing conventional solvents which produce VOC emissions.

Vernonia oil contains predominantly (~80 percent) trivernolin, a triglyceride of vernolic acid (Figure 1). Vernonia oil is a naturally occurring epoxidized vegetable oil containing three epoxy rings and three carbon double bonds per triglyceride molecule. There is one epoxy ring and one carbon-carbon double bond per each vernolic acid residue.

Figure 1. Molecular structure of triolein, vernonia oil and epoxidized soybean oil.



Vernonia Galamensis

Vernonia galamensis, the source of vernonia oil, is a new potential oil seed crop in Africa, Asia, Central America and in the Southwest U.S.A., in the dry areas of Arizona, New Mexico, etc. (Ref. 1-6). *Vernonia galamensis* grows in both arid and semi-arid areas of the tropics and sub-tropics on land that is practically unsuitable for food crops. It is an annual herb, as common as a weed in West Africa, that can be harvested directly. It has good seed retention and the seeds mature uniformly and germinate easily, which is important for crop utilization. It also has a natural resistance to diseases, nematodes, and insects. Neither wild nor domestic animals consume *Vernonia galamensis*.

Vernonia seeds contain about 42 percent oil in contrast to soybean seeds, which contain only 17 percent oil. The maximum seed yield reached at this development stage of *Vernonia galamensis* is 2,227 pounds per acre. Unfortunately, it has not been reproduced. Increased yield of vernonia oil, however is expected by breeding as greater genetic diversity becomes available and by better management of the crop. The best soybean seed yield is 1,926 pounds per acre (1979), which was the best soybean oil year in the U.S. after about 50 years of cultivation. Dr. R. Perdue from the U.S. Department of Agriculture expects similar seed yields for soybean and *Vernonia galamensis* after crop maturity.

In summary, it appears that the major agronomic problems for *Vernonia galamensis'* cultivation have been resolved. *Vernonia galamensis* is at a de-

velopmental stage at the present moment in several African countries, especially in Zimbabwe and Kenya; and has a potential to soon become an industrial crop. Several major chemical and coatings companies have expressed strong interest in vernonia oil. Hi-Tek Polymers Inc. has started experimental crop trials for vernonia oil production, and several tons of *Vernonia galamensis* seeds are expected to be harvested next year. Cargill is evaluating the possibilities for cultivation of *Vernonia galamensis* and the potential use of vernonia oil as well.

Results and Discussion

Vernonia oil has several unique features:

- It is a transparent homogeneous liquid at room temperature with excellent solubility in many organic solvents, diluents, and paints.
- Vernonia oil has a low viscosity of 300 cps at 50°F and 100 cps at 85°F.
- It has a low melting point of ~36°F.
- Vernonia oil has a homogeneous molecular structure consisting predominantly of identical triglyceride molecules which have three equal vernolic acid residues. In contrast, all other vegetable oils consist of a heterogeneous mixture of triglycerides with different fatty acid residues.
- It is expected to be available at a low price of approximately 45 to 75 cents per pound.
- Toxicity of vernonia oil is expected to correspond to that of the epoxidized soybean and linseed oils which are industrially produced.

Vernonia Vs. Other Epoxidized Vegetable Oils. Vernonia oil does not compete with other epoxidized vegetable oils, i.e. epoxidized soybean oil and epoxidized linseed oil, which are industrially produced by epoxidation of unsaturated vegetable oils and have structures similar to vernonia oil. Epoxidized soybean and linseed oils are not suitable for coatings applications as reactive diluents based on their higher viscosity, or at least they are less suitable than vernonia oil. Both epoxidized soybean oil and linseed oils have higher viscosity, i.e. in the range of 1,000-2,000 cps at 50°F, in contrast to 300 cps for vernonia oil. Both are heterogeneous semi-solids even at 75°F and form homogeneous, clear liquids only above 85°F. Their applications require a warming procedure at 120°F with mild agitation prior to use for at least one hour.

In addition, the price of the epoxidized soybean and linseed oils is significantly higher than the expected price of the naturally occurring epoxidized vernonia oil. The price of soybean oil, which is about 25 cents per pound, increases to $1.36 per pound for the epoxidized soybean oil. Epoxidized linseed oil is even more expensive.

The difference in viscosity of vernonia oil and epoxidized soybean oil is rather surprising even though both oils have similar molecular structures. Initially, we thought that soybean oil partially polymerizes during the epoxidation reaction and the resulting epoxidized soybean oil contains oligomers which increase its viscosity. GPC of vernonia oil and eoxidized soybean oil, however, are identical (Figure 2). Evidently, both oils have exactly the same molecular weight distribution and the low viscosity is an inherent characteristic of vernonia oil.

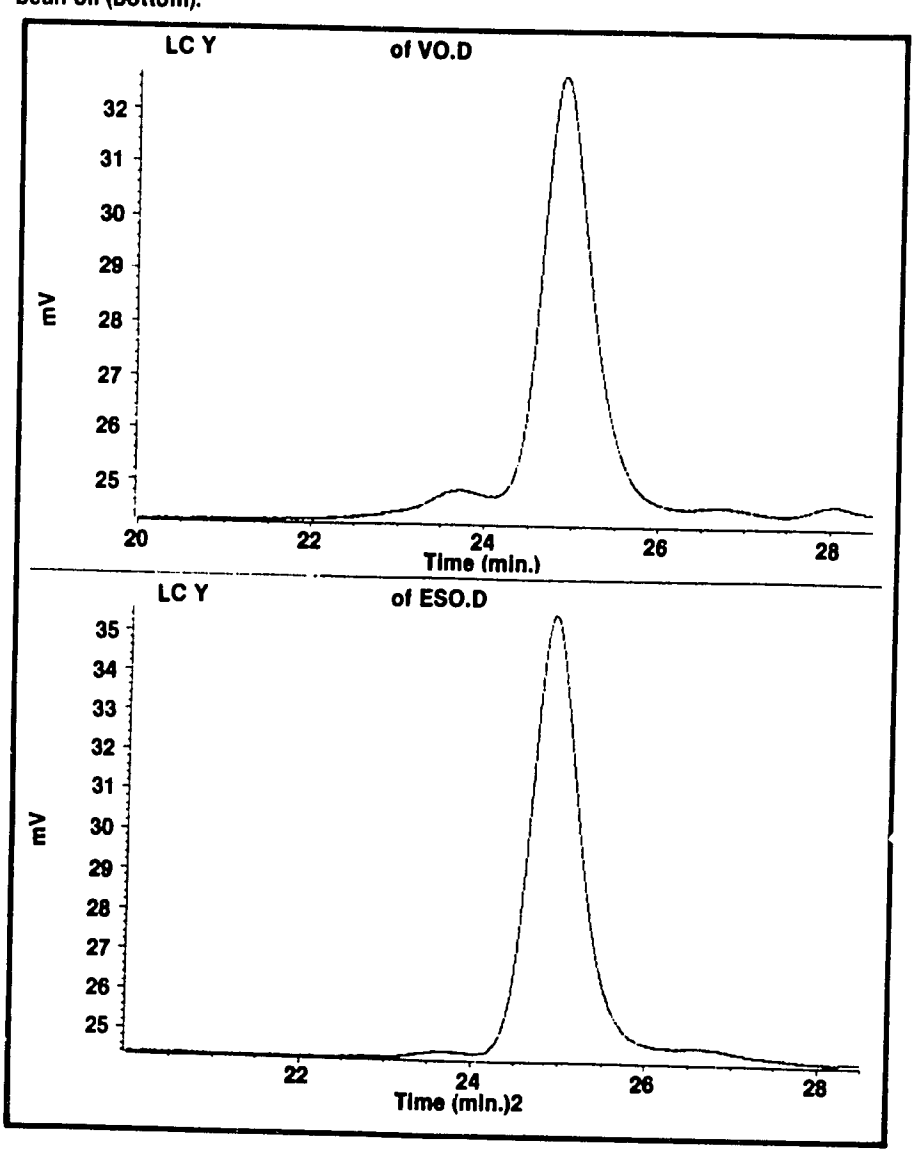
Drying Mechanism of Vernonia Oil. Ken Carlson and co-workers (Ref. 7) have reported that vernonia coatings can be obtained directly from vernonia oil by a standard baking procedure at 150° for 30 minutes in the presence of different drier systems.

We were interested in the drying mechanism of vernonia oil since it has two functionalities: unsaturated double bond and epoxy ring. For this purpose, we have compared the drying characteristics of triolein, vernonia oil, and epoxidized soybean oil in the presence of 0.5 per cent cobalt drier under baking conditions at 150°C for one hour. The molecular structure of these three oils is shown in Figure 1.

Epoxidized soybean oil does not form coatings at 185°C for several hours. Obviously, its epoxy groups do not polymerize under these conditions.

Both triolein and vernonia oil form good coatings. These results show that vernonia oil drying is based on its unsaturated carbon-carbon double bonds

Figure 2. Gel permeation chromatography of vernonia oil (top) and epoxidized soybean oil (bottom).



and not on its epoxy functionality. This allows its application as a reactive diluent, not only in epoxy and epoxy-ester formulations, but in alkyd resins as well.

Results also show that vernonia oil dries at lower temperature and much faster than the triolein. Good coatings have been obtained from vernonia oil at 150°C for half an hour. Triolein does not form coatings at 150°C for one hour. It forms coatings only at 180°C for 1.5 hours. The epoxy rings of vernonia oil probably activated the oxidation of the methylene group between the epoxy ring and the carbon-carbon double bond and, therefore, faster drying is observed in comparison to triolein.

Table I. Composition Of Paint Formulations In Weight Parts

10-060 L.O. Alkyd	78.60
Odorless Mineral Spirits	23.59
BYK Bykumen	3.77
Nuodex Nuxtra Calcium 10%	1.12
Premix Above	
DuPont R-900 TiO2	150.97
T & W Atomite	37.74
NL Chemical SD-1 Bentone	2.72
Add Slowly to Cowles	
10-060 L.O. Alkyd	81.62
Vernonia Oil	
Add To Grind	
Nuodex Nuxtra Cobalt 12%	0.46
Nuodex Nuxtra Zirco 24%	2.34
Odorless Mineral Spirits	93.10
Nuodex Exkin #2	1.62
Premix Then Add	

Table II. Driers For Vernonia Oil And Long Oil Alkyd

Cobalt Naphthenate
Zirconium Drier
Manganese Drier
Calcium Drier

Drier Combinations
- Mooney Driers: Co, Ca, DRI-Rx
- Mooney Driers: Co, Mn, DRI-Rx
- Nuodex Nuxtra Cobalt
- Nuodex Nuxtra Zirco
- Nuodex Nuxtra Calcium
- Nuodex ADR
  - Blended Metals/Surface Drier
- Nuodex LTD
  - Complex Of Metals/Through Drier
- Nuodex UTD
  - Complex Of Metals/Through Drier
- Activ 8
  - Drier Stabilizer And Accelerator
- Manchem Manosec CD-44
  - Cobalt Drier

Table III. Characterization Of Clear Coatings Prepared Under Baking Conditions: Cobalt Drier 0.04%, 150°C, 1 hr., On Cold Rolled Steel Panel, 2 Mil Thickness

	Vernonia Oil	Alkyd (80%) Vernonia Oil (20%)	Alkyd 10-560 10-060
Adhesion	4B	4B	4B
Hardness:			
Pencil	H	2H	H
Rocker	42	42	46
Flexibility	Excellent	Excellent	Excellent
Impact Strength:			
Direct, lb. in.	150	150	160
Reverse, lb. in.	140	140	145

Compatibility with Alkyd Resins. Compatibility studies have been carried out with Reichhold Beckosol long oil alkyds 10-560 and 10-060, medium oil alkyd 11-035, and short oil alkyd 12-005. Vernonia oil is compatible with all three types of alkyd resins at any ratio.

Drier Evaluation. Evaluations were made for different driers and drier combinations for vernonia oil and for its 20 percent mixtures in alkyd resins (Table II). Cobalt drier at 0.1 percent concentration forms good coatings at 150°C for one hour. Zirconium drier even at higher concentration (0.5 percent) does not form coatings at higher temperature (160°C) and longer time (two hours). Calcium and manganese driers have intermediate activity, weaker than the cobalt drier but stronger than the zirconium. Without going into further detail, Manchem Manosec CD-44 drier gives the best results. It is more active than all other driers and drier combinations. It contains cobalt (0.6 percent), calcium (0.2 percent), and lithium (0.03 percent) carboxylates in mineral spirits.

Vernonia oil does not air-dry with any of the driers at room temperature in several hours. In the presence of Manosec CD-44 it dries slowly in about a week. However, alkyd resin mixtures containing 10 to 40 percent vernonia oil air-dry at room temperature within several hours.

Clear Coatings. Table III compares the properties of the 2 mil thick coatings obtained under baking conditions in the presence of 0.04 percent cobalt naphthenate drier at 150°C for one hour on cold rolled steel panels from vernonia oil, pure 10-560 and 10-060 long oil alkyds, and their mixture containing 20 per cent vernonia oil.

All coatings have good adhesion of 4B. Hardness is also good. Pencil hardness is H and Rocker Sward hardness is 42. Both adhesion and hardness improve at higher baking temperature and longer time. Flexibility, according to a standard test by bending the steel panel around 180°, is excellent. We did not observe any cracks or tape-off under microscope. The impact strength is also excellent. The direct impact strength is 150 pounds/inch, whereas the reverse is 140 pounds/inch.

All three types of coatings have the same properties which indicates that introduction of vernonia oil does not deteriorate the basic properties of alkyd resin.

Long Oil Alkyd Paint Formulations. We also prepared a typical paint formulation shown on Table I and com-

pared it to the paint formulations in which the initial long oil alkyd has been substituted with 20 and 40 percent vernonia oil. Table IV compares the Brookfield viscosity, RCI drying times in hours at room temperature of coatings with 3 mil thickness, and VOC in pounds per gallon.

The first paint formulation corresponds to the initial formulation based only on alkyd resin (Table I).

In the second paint formulation, 20 percent of the alkyd has been substituted with vernonia oil. Lower viscosity is observed for this formulation.

The next two formulations contain 20 percent vernonia oil but their solvent content has been gradually reduced. The goal is to decrease the solvent to the point at which the viscosity of the paint formulation corresponds to the viscosity of the initial paint formulation without vernonia oil. These two formulations have much lower volatiles.

The fifth paint formulation is exactly as the first one with the only difference being that it contains the new, more active CD-44 drier. Drying time of the paint formulations or tack-free time changes very little in the presence of vernonia oil, but sharply decreases in the presence of CD-44.

Finally, the last formulation contains the new drier system and 20 percent of its alkyd resin has been substituted with vernonia oil. The important result here is that by introducing 20 percent vernonia oil in this formulation we are able to decrease the volatiles, and thus eventually reduce air-pollution, reduce the drying time, and maintain equal or lower viscosity than the initial paint formulation.

A potential problem for direct application of vernonia oil in alkyd formulations is an anticipated reaction between its epoxy groups and the terminal carboxyl groups of the alkyd resins. Our results show that vernonia oil does not change the can stability of the formulations. Obviously, the epoxy groups of vernonia oil have low reactivity and do not react with the free carboxyl groups of the alkyd resins under test conditions for can stability. The low reactivity of the epoxy groups of vernonia oil has been confirmed by additional experiments.

The QUV test, which measures decrease in gloss at 20° and 60° after exposure at UV light and humidity for a week, indicates that vernonia oil improves the coatings weatherability.

Medium Oil Alkyd Paint Formulations. The effect of vernonia oil on paint formulations and coatings based on medium oil alkyd resin Reichhold Aroplaz 6440 is similar to that described above for long oil alkyds.

Epoxy Coatings. Vernonia oil contains reactive epoxy groups and our initial results show that it is an attractive reactive diluent for epoxy or epoxy ester formulations as well. Another possibility, again for epoxy formulations, is transesterification of vernonia oil with methanol or other higher molecular weight mono-functional alcohols for preparation of very low viscosity diluents. For example, methyl vernolate shown in Figure 3 has been prepared with quantitative yield. Similar esters are industrially produced and the U.S. Navy has used them for coatings aplications under water. However, they are very expensive.

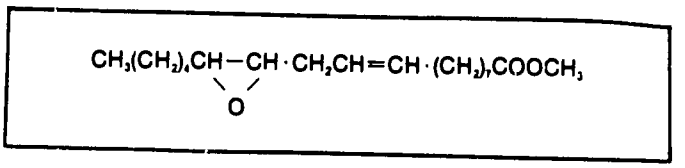


Figure 3. Molecular structure of methyl vernolate.

Table IV. Characterization Of Paint Formulation

Paint Formulation	Brookfield Viscosity cps	RCI Drying Time, Hr	VOC Lb./Gal.
1. Initial 10-060	2640	13	3.15
2. V.O. 20%	586	11	3.11
3. V.O. 20% Less Solvent	2260	15	2.63
4. V.O. 20% Less Solvent	3476	12	2.52
5. Initial 10-060 Drier CD-44	3344	3-4	2.50
6. Drier CD-44 V.O. 20%	780	4	2.60

Experimental

Vernonia oil has been kindly supplied by Dr. K. Carlsen from the U.S. Department of Agriculture. Its extraction from *Vernonia galamensis* seeds, refining and characterization is described in Ref. 7 The preparation of the coatings formulations is shown in Table I. The characterization of these formulations and their final coatings has been carried out according to the corresponding ASTM methods.

Conclusion

Vernonia oil, a naturally occuring epoxidized vegetable oil at developmental stage, has a unique structure with reactive epoxy rings, double bonds, lower viscosity than other epoxidized vegetable oils and a low melting point. It is an attractive reactive diluent for preparation of high solids alkyds and epoxy coating formulations.

Acknowledgment

We would like to gratefully acknowledge the financial support by the South Coast Air Quality District Management, U.S. Agency for International Development, the Paint Research Associates, and Michigan State. We also thank Dr. John C. Graham, Coatings Research Institute and Dr. Robert Perdue from the U.S. Department of Agriculture for advice and many fruitful discussions.

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POLYMERS PAINT

RESINS & PIGMENTS '90

IN THIS ISSUE: RESINS FOR PAINT & PRINTING INKS

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RESINS

Vernonia Oil: A reactive diluent for alkyd and epoxy resins and coatings

by S DIRLIKOV, M ISLAM, I FRISCHINGER, T LEPKOWSKI, and P MUTURI

There is a strong need for reactive diluents, to help in the reduction of conventional non-reactive solvents in coating formulations for reasons of air pollution control. Recently, further and stricter measures have been taken for reduction of air pollution. In 1988, the US Environmental Protection Agency announced a ban on construction of major air-polluting plants in Los Angeles and other US cities, and in the same year the South Coast Air Quality District Management announced a plan for reduction of hydrocarbon emission in Orange County, California by 80-90% over the next five years. This plan requires reduction of volatile organic compound (VOC) emission from paints and varnishes from the current 22.1 tons per day to 2.9 tons per day several years from now. It is an impossible task with today's coatings technology.

The objective of this research is the application of vernonia oil as a reactive diluent for high solids alkyd, epoxy, and epoxy-ester coating formulations by replacing conventional solvents which produce VOC emission.

Vernonia oil contains predominantly (~80%) trivernolin, a triglyceride of vernolic acid (Fig 1). Vernonia oil is a naturally occurring epoxidized vegetable oil containing three epoxy rings and three carbon-carbon double bonds per triglyceride molecule. There is one epoxy ring and one carbon-carbon double bond for each vernolic acid residue.

VERNONIA GALAMENSIS

Vernonia galamensis, the source of vernonia oil, is a new potential oil seed crop in Africa, Asia, Central America and in the Southwest USA, in the dry areas of Arizona, New Mexico, etc.[1-6]. *Vernonia galamensis* grows in both arid and semi-arid areas of the tropics and sub-tropics on land that is practically unsuitable for food crops. It is an annual herb, as common as a weed in West Africa, that can be harvested directly. It has good seed retention and the seeds mature uniformly and germinate easily, which is very important for crop utilization. It also has a natural resistance to disease, nematodes, and insects. Neither wild nor domestic animals consume *Vernonia galamensis*.

"Vernonia" seeds contain about 42% of oil in contrast to soybean seeds, which contain only 17% oil. The maximum seed yield reached at this development stage of *Vernonia galamensis* is 2227 pounds per acre[2]. Unfortunately, it has not been reproduced. Increased yield of vernonia oil, however, is expected by breeding as greater genetic diversity becomes available and by better management of the crop. The best soybean seed yield is 1926 pounds per acre (1979), which was the best soybean oil year in the US after about fifty years of cultivation. Dr R. Perdue from the US Department of Agriculture expects similar seed yields for soybean and *Vernonia galamensis* after crop maturity.

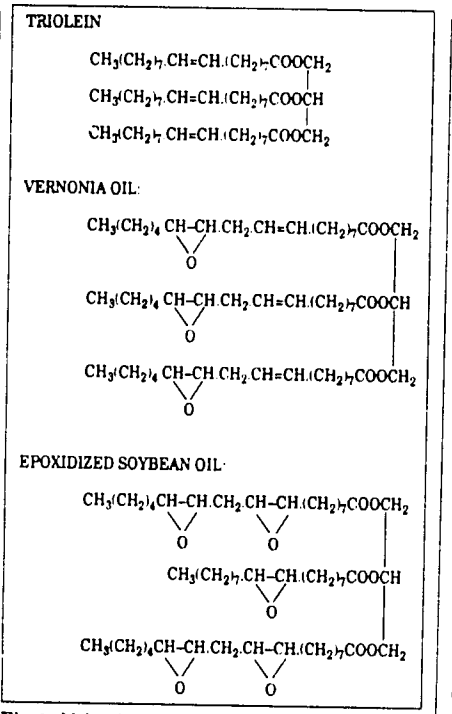

Fig 1: *Molecular structure of triolein, vernonia oil, and epoxidized soybean oil*

In summary, it appears that the major agronomic problems for *Vernonia galamensis'* cultivation have been resolved. *Vernonia galamensis* is at a developmental stage at present in several African countries, especially in Zimbabwe and Kenya; and has the potential to soon become an industrial crop. Several major chemical and coatings companies have expressed strong interest in vernonia oil. Rhone-Poulenc (USA division) has started experimental crop trials for vernonia oil production, and several tons of *Vernonia galamensis* seeds are being harvested this year. Cargill is evaluating the possibilities for cultivation of *Vernonia galamensis* and the potential use of vernonia oil as well.

RESULTS AND DISCUSSION

Properties of Vernonia Oil

Vernonia oil has several unique features:

- It is a transparent homogenous liquid at room temperature with excellent solubility in many organic solvents, diluents, and paints.
- Vernonia oil has a low viscosity of 300 cps at 50°F and 100 cps at 85°F.
- It has a low melting point of −36°F.
- Vernonia oil has a homogenous molecular structure consisting predominantly of identical triglyceride molecules which have three equal vernolic acid residues. In contrast, all other vegetable oils consist of a heterogeneous mixture of triglycerides with different fatty acid residues.
- It is expected to be available at a low price in the range of $1.00-1.50 per pound.
- Toxicity of vernonia oil is expected to correspond to that of the epoxidized soybean and linseed oils which are industrially produced.

Vernonia vs. Other Epoxidized Vegetable Oils

The authors believe that vernonia oil does not compete with other epoxidized vegetable oils, ie, epoxidized soybean oil and epoxidized linseed oil, which are industrially produced by epoxidation of unsaturated vegetable oils and have structures similar to vernonia oil. Epoxidized soybean and linseed oils are not suitable for coatings applications as reactive diluents due to their higher viscosity, or at least they are less suitable than vernonia oil.

Both epoxidized soybean oil and linseed oils have higher viscosity, ie, in the range of 1000-2000 cps at 50°F, in contrast to 300 cps for vernonia oil. Both are heterogeneous semi-solids even at 75°F and form homogeneous, clear liquids only above 85°F. Their applications require, prior to use, a warming procedure at 120°F with mild agitation for at least one hour.

The difference in viscosity of vernonia oil and epoxidized soybean oil is rather surprising even though both oils have similar molecular structures. Initially, we thought that soybean oil partially polymerized during the epoxidation reaction and the resulting epoxidized soybean oil contained a certain amount of oligomer which increased its viscosity. GPC of vernonia oil and epoxidized soybean oil, however are identical (Fig 2). Evidently, both oils have exactly the same molecular weight distribution and the low viscosity is an inherent characteristic of vernonia oil.

Table 1: *Composition of paint formulations in weight parts*

10-060 Long oil alkyd	78.60
Odourless mineral spirits	23.59
BYK Bykumen	3.77
Nuodex *Nuxtra* Calcium 10%	1.12
Premix above	
DuPont *R-900 TiO2*	150.97
T & W Atomite	37.74
NL Chemical *SD-1 Bentone*	2.72
add slowly to cowls	
10-060 Long oil alkyd	81.62
Vernonia oil	
add to grind	
Nuodex *Nuxtra* cobalt 12%	0.46
Nuodex *Nuxtra* zirco 24%	2.34
Odourless mineral spirits	93.10
Nuodex *Exkin #2*	1.62
Premix then add	

Continued on page 668

RESINS

Drying Mechanism of Vernonia Oil

[illegible] and co-workers[7] have reported [illegible] coatings can be obtained direct- [illegible] vernonia oil by a standard baking [illegible] at 150 for 30 minutes in the presence of different drier systems.

The authors were interested in the drying mechanism of vernonia oil since it has two functionalities: an unsaturated double bond and an epoxy ring. For this purpose, they compared the drying characteristics of triolein, vernonia oil, and epoxidized soybean oil in the presence of 0.5% cobalt drier under baking conditions at 150°C for one hour. The molecular structure of these three oils is shown in Figure 1.

Epoxidized soybean oil did not form coatings at 185°C for several hours. Obviously its epoxy groups do not polymerize under these conditions.

Both triolein and vernonia oil formed good coatings. These results show that vernonia oil drying is based on its unsaturated carbon-carbon double bonds and not on its epoxy functionality. This allows its application as a reactive diluent, not only in epoxy and epoxy-ester formulations, but in alkyd resins as well.

Results also showed that vernonia oil dries at lower temperature and much faster than the triolein. Good coatings were obtained from vernonia oil at 150°C for half an hour. Triolein did not form coatings at 150°C for 1 hour. It formed coatings only at 180°C for 1.5 hours. The epoxy rings of vernonia oil probably activate the oxidation of the methylene group between the epoxy ring and the carbon-carbon double bond and we, therefore observed its faster drying in comparison to triolein.

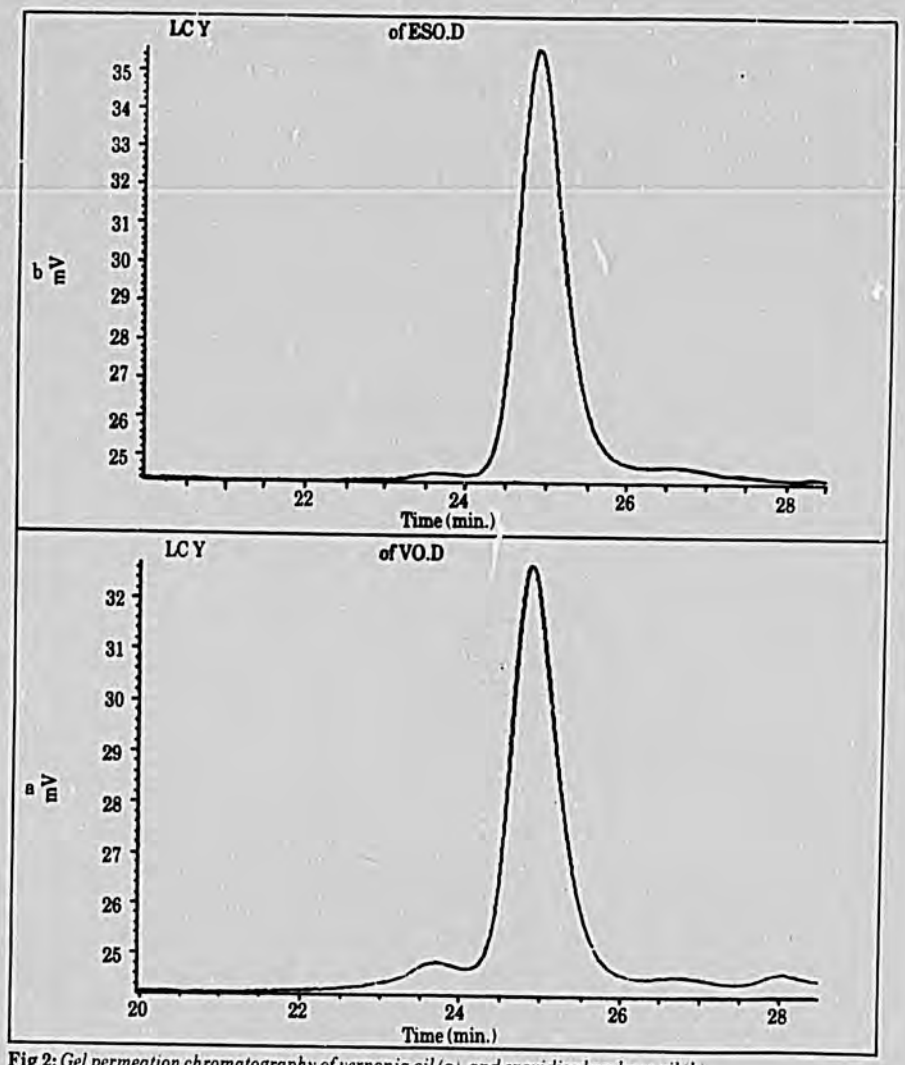

Fig 2: *Gel permeation chromatography of vernonia oil (a), and epoxidised soybean oil (b)*

Compatibility with Alkyd Resins

Compatibility studies have been carried out with Reichhold *Beckosol* long oil alkyd 10-560 and 10-060, medium oil alkyd 11-035, and short oil alkyd 12-005. Vernonia oil is compatible with all three types of alkyd resins at any ratio.

Drier Evaluation

Different driers and drier combinations for vernonia oil and for its 20% mixtures in alkyd resins (Table 2) were evaluated. Cobalt drier at 0.1% concentration formed good coating at 150°C for 1 hr. Zirconium drier even at higher concentration (0.5%) did not form coatings at higher temperature (160°C) and longer time (2 hours). Calcium and manganese driers had intermediate activity, weaker than the cobalt drier but stronger than the zirconium. Without going into further detail, Manchem *Manosec CD-44* drier gave the best results. It was more active than all other driers and drier combinations. It contains cobalt (0.6%), calcium (0.2%), and lithium (0.03%) carboxylates in mineral spirits.

Vernonia oil did not air dry with any of the driers at room temperature in several hours. In the presence of *Manosec CD-44* it dried slowly in about a week. However, alkyd resin mixtures containing 10-40% vernonia oil air-dried at room temperature within several hours.

Clear Coatings

Table 3 compares the properties of the 2 mil thick coatings obtained under baking conditions in the presence of 0.04% cobalt naphthenate drier at 150°C for one hour on cold rolled steel panels from vernonia oil, pure 10-560 and 10-060 long oil alkyds, and their mixture containing 20% vernonia oil.

All coatings have good adhesion of 4B. Hardness was also good. Pencil hardness was H and Rocker Sward hardness was 42. Both adhesion and hardness improved at higher baking temperature and longer time. Flexibility, according to a standard test by bending the steel panel around 180°, was excellent. No cracks or tape-off was observed under a microscope. The impact strength was also excellent. The direct impact strength was 150 pounds inch., whereas the reverse was 140 pounds inch.

All three types of coatings had the same properties which indicates that introduction of vernonia oil does not deteriorate the basic properties of alkyd resin.

Table 2: *Driers for Vernonia Oil and Long Oil Alkyd*

Cobalt naphthenate
Zirconium drier
Manganese drier
Calcium drier
Drier combinations
Mooney driers: Co, Ca, *DRI-Rx*
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Nuodex *Nuxtra* Zirco
Nuodex *Nuxtra* Calcium
Nuodex ADR
Blended metals/surface drier
Nuodex Ltd
Complex of metals/through drier
Nuodex UTD
Complex of metals/through drier
Activ 8
Drier stabilizer and accelerator
Manchem *Manosec CD-44*

Long Oil Alkyd Paint Formulations

A typical paint formulation was prepared shown in Table 1 and compared to the paint formulations in which the initial long oil alkyd was substituted with 20 and 40% vernonia oil. Table 4 shows comparison of the *Brookfield* viscosity, RCI drying times in hours at room temperature of coatings with 3 mil thickness, and VIC in lb. per gallon.

The first paint formulation corresponds to the initial formulation based only on alkyd resin (Table 1). In the second paint formulation, 20% of the alkyd was substituted with vernonia oil. Lower viscosity was observed for this formulation.

The next two formulations still contain 20% vernonia oil but their solvent content was gradually reduced. The goal being to decrease the solvent to the point at which the viscosity of the paint formulation corresponds to the viscosity of the initial paint formulation without vernonia oil. These two formulations had much lower volatiles.

The fifth paint formulation was exactly as the first one with the only difference being that it contained the new, more active *CD-44* drier. Drying time of the paint formulations

or tack-free time changed very little in the presence of vernonia oil, but sharply decreased in the presence of *CD-44*.

Finally, the last formulation contained the new drier system and 20% of its alkyd resin had been substituted with vernonia oil. The important result here is that by introducing 20% vernonia oil in this formulation it was possible to decrease the volatiles, and thus eventually reduce air-pollution, reduce the drying time, and maintain equal or lower viscosity than the initial paint formulation.

A potential problem for direct application of vernonia oil in alkyd formulations was an anticipated reaction between its epoxy groups and the terminal carboxyl groups of the alkyd resins. The results show that vernonia oil did not change the can stability of the formulations. Obviously, the epoxy groups of vernonia oil have low reactivity and do not react with the free carboxyl groups of the alkyd resins under test conditions for can stability. The low reactivity of the epoxy groups of vernonia oil was confirmed by additional experiments.

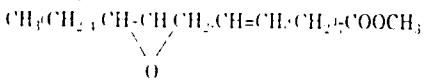
Q-UV test, which is the decrease in gloss at 20° and 60° after exposure at UV light and humidity for a week, indicated that vernonia oil improved the coatings weatherability.

Medium Oil Alkyd Paint Formulations

The effect of vernonia oil on paint formulations and coatings based on medium oil alkyd resin Reichhold *Aroplaz 6440* was similar to that described above for long oil alkyds.

Epoxy Reactive Diluents

Vernonia oil contains reactive epoxy groups and the initial results showed that it is an attractive reactive diluent for epoxy or epoxy ester formulations as well. Another possibility, again for epoxy formulations, is transesterification of vernonia oil with methanol or other higher molecular weight monofunctional alcohols for preparation of very low viscosity diluents. For example, methyl vernolate shown here has been prepared in quantitative yield:



Similar esters are industrially produced and the US Navy has used them for coatings applications under water. However, they are very expensive.

Modification of Epoxy Resins and Coatings

The second part of the project is on application of vernonia oil for modification of commercially available epoxy resins and coatings. The project objective is simultaneous improvement of the two main disadvantages of epoxy resins: low toughness and high water absorption.

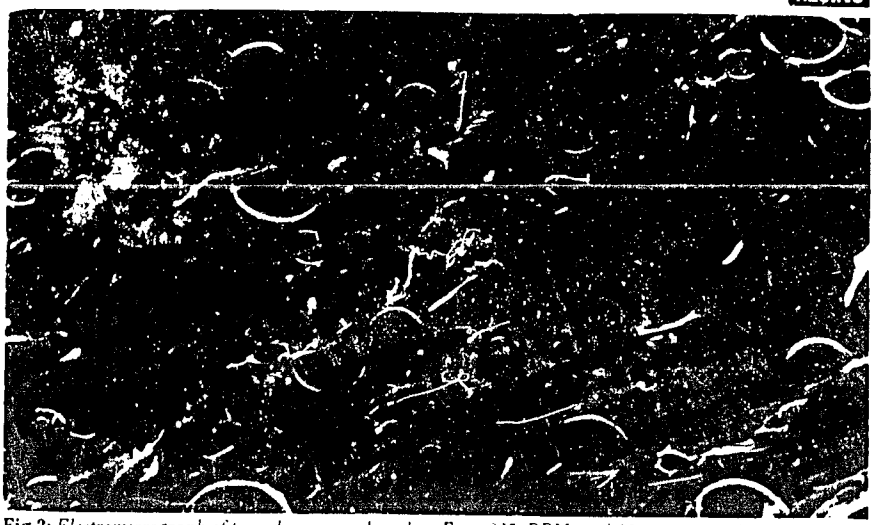


Fig 3: *Electromicrograph of two-phase epoxy based on Epon 825, DDM, and 20% vernonia dodecanediamine B-staged material.*

It is known that a small amount of discrete rubbery particles with an average size of several microns, randomly distributed in a glassy, brittle epoxy resin, dissipates part of the impact energy thus improving crack and impact resistance without deterioration of other properties of the initial epoxy resins.

The epoxy resin toughness is usually achieved by separation of a rubbery phase with a unimodal size distribution from the matrix during the curing process. Different carboxy- or aminoterminated (butadiene, siloxane, etc.) oligomers are used for the formation of the rubbery phase. Some of these oligomers are quite expensive. Vernonia oil, however, opens new opportunities. The epoxy resins based on vernonia oil and commercial amines are elastomers at room temperature. They have low glass transition temperatures, in the range of −80 C to 0 C, which depends on the nature of the diamine used for curing of vernonia oil. They appear to be very suitable for toughening of commercial epoxies.

It has been possible to obtain two-phase epoxy thermosets and coatings with rubbery vernonia particles by using vernonia B-staged materials as described in the experimental section. For this purpose, vernonia oil was initially B-staged with DDM or 1,12-dodecanediamine. Then homogenous mixtures of commercial epoxy resin (*EPON 825*) and commercial amines (DDS, DDM, isophorone diamine, different aliphatic di- and polyamines, etc.), containing 10 to 25% vernonia oil B-staged material were cured according to a 'standard' curing procedure for epoxy resin. Commercial epoxy resins have higher reactivity with commercial diamines than the epoxy groups of vernonia oil. As a result, they formed a rigid matrix at 70 C in which vernonia liquid droplets, phase separate. The final thermoset was cured at 150 C. It consisted of a rigid epoxy matrix with randomly distributed small rubbery 'vernonia' spherical particles (Fig 3). Diamine molecules at the interface are expected to react with both the epoxy groups of the commercial epoxy resin and the unreacted epoxy groups of vernonia oil, and will presumably form a chemical bond between the rigid matrix and the rubbery particles.

Several factors control phase separation. Miscibility of the initial mixture of epoxy resin, amine, and vernonia oil or its B-staged material, is required. Incompatibility and phase separation should start during the curing process before gelation for spherical morphology formation. Simultaneously, viscosity at this stage should be high to prevent coalescence and microscopic phase separation. The effective rubbery phase depends on the volume fraction of vernonia oil, nature of curing amine, and time and temperature regime of cure.

The particle diameter is a function of the incompatibility of vernonia B-staged material and the epoxy matrix. We have been able to vary the particle diameter in the range of the desirable particle size for toughening thermosets, eg, 0.3 to 50 microns. In general, larger particles were obtained for less compatible systems with more popular diamines, for instance, with DDS for curing of the rigid matrix. The electromicrograph of an epoxy thermoset, based on *EPON 825*, DDM, and 20% of vernonia oil, dodecanediamine B-staged material, shows vernonia rubbery particles with a broad distribution in the range of 5 to 30 microns diameter (Fig 3). The glass transition temperatures of the rubbery phase and the rigid epoxy matrix of this thermoset are observed in DMA at −22 and [illegible] respectively (Fig 4). Cont[illegible]

Table 3: *Characterization of clear coatings prepared under baking conditions: Cobalt drier 0.04%, 150 C, 1 hr, on cold rolled steel panel, 2 mil thickness.*

	Vernonia Oil	Alkyd (80%) Vernonia Oil (20%)	Alkyd 10-560 10-060
Adhesion	4B	4B	4B
Hardness:			
Pencil	H	2H	H
Rocker	42	42	46
Flexibility	Excellent	Excellent	Excellent
Impact Strength:			
Direct, lb·in	150	150	160
Reverse, lb·in	140	140	145

Table 4: *Characterization of paint formulation*

	Paint Formulation	Brookfield Viscosity CPS	RCI Drying Time, Hr	VOC lb/gal.
1	Initial 10-060	2640	13	[illegible]
2.	V.O. 20%	586	11	[illegible]
3	V.O. 20% Less solvent	2260	15	[illegible]
4	V.O. 20% Less solvent	3476	12	[illegible]
5	Initial 10-060 Drier *CD-44*	3344	3-4	[illegible]
6	Drier *CD-44* V.O. 20%	780	4	[illegible]

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Appendix I: *Moisture vapour barrier primer/sealer formulation, PVC=60%*

Material		Weight
Water		250.0
Nopco NDW	(Diamond Shamrock)	2.0
Propylene glycol	(Dow Chemical)	20.0
Natrosol 250 HHBR	(Aqualon)	3.0
Triton X-100	(Rohm & Haas)	2.0
AMP-95	(Angus Chemical Co.)	4.0
DOWICIL 75	(Dow Chemical)	1.0
Ti-Pure R-900	(DuPont)	100.0
Duramite	(Thibaut & Walker Co.)	220.0
Huber-80	(J.M. Huber Co.)	140.0
Nopco NDW	(Diamond Shamrock)	2.0
DOWANOL PPh	(Dow Chemical)	9.0
Modified S/B	(Dow Chemical)	200.00
Water		176.00
		1129.0

Appendix II: *Tannin block primer/sealer formulation, PVC=40%*

Material		Weight
Water		235.0
KTPP	(FMC)	1.5
Nopco NDW	(Diamond Shamrock)	1.0
Propylene glycol	(Dow Chemical)	21.5
DOWANOL DPnB	(Dow Chemical)	10.0
SCT-275	(Union Carbide)	16.5
Surfynol 104E	(Air Products)	4.0
AMP-95	(Angus Chemical Co)	4.0
DOWICIL 75	(Dow Chemical)	1.0
Tronox CR-821	(Kerr/McGee)	150.0
Halox BW-100	(Hammond Lead)	50.0
Duramite	(Thibaut & Walker Co.)	200.0
XX-503 ZnO	(New Jersey Zinc)	25.0
Nopco NDW	(Diamond Shamrock)	1.0
Modified S/B	(Dow Chemical)	425.0
		1145.5

Vernonia Oil

Continued from page 669

The initial results show improved fracture toughness (K_{IC}), impact resistance and low water absorption for thus modified epoxy resins and coatings.

EXPERIMENTAL

Vernonia oil was kindly supplied by Dr K Carlson from the US Department of Agriculture. Its extraction from *Vernonia galamensis* seeds, refining and characterization has been described[7]. The preparation of alkyd coatings formulations is shown in Table 1. The characterization of these formulations and their final coatings were carried out according to the corresponding ASTMs.

Two-phase epoxy thermosets and coatings were prepared from vernonia oil which was initially B-staged with amines. For this purpose a mixture of 100g of vernonia oil and 25.63g of 4,4'-methylenedianiline (DDM) were heated at 180°C for 40 hours under nitrogen. Similar results were observed for vernonia B-staged material obtained from 25.9 g of 1,12-dodecanediamine and 100 g of vernonia oil under the same conditions. The vernonia B-staged material based on DDM or 1,12-dodecanediamine was added in 10, 20 or 30 weight percent to a stoichiometric mixture of diglycidyl ether of bisphenol A (Shell epoxy resin *Epon 825*) and DDM or 4-aminophenyl sulphone (DDS). The resulting DDM homogeneous formulation was additionally B-staged at 75°C for 95 minutes under nitrogen, and then poured into the casting mould and placed under vacuum. Final cure and post-cure were carried out at 75°C for four hours and 150°C for two hours, respectively. The corresponding DDS formulation was B-staged at 150°C for one hour under nitrogen and then cured in the mould at 150°C for two hours. Both DDM or DDS formulations produced excellent large castings. Electromicrographs were taken by an Amray electron microscope, model 1000B.

CONCLUSION

Vernonia oil, a naturally occurring epoxidized vegetable oil at developmental stage, has a unique structure with reactive epoxy rings, double bonds, lower viscosity than other industrially produced epoxidized vegetable oils, and a low melting point. It is an attractive reactive diluent for preparation of high solids alkyds and epoxy coating formulations.

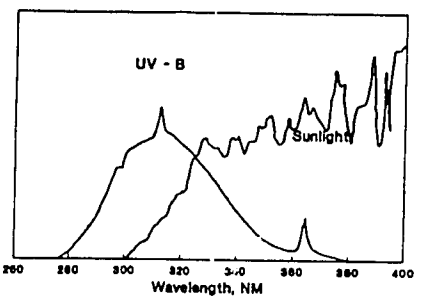

Fig 5: *UV – B vs Sunlight*

and Tannin Block primer/sealer applications. Field trials show promising results for interior topcoat applications, but the exposure time is too short to recommend these binders yet for exterior topcoat applications.

As a class, modified styrene butadienes exhibit excellent moisture vapour barrier, hydrolytic stability and high binder efficiency.

Mrs V Stevens is with Dow Chemical USA, Midland, Michigan and Dr P Griggs is with Dow Europe, Horgen, Switzerland

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7. K. D. Carlson, W. J. Schneider, S. P. Chang & L. H. Princen in: "New Sources of Fats & Oils", AOCS Monograph No. 9, E. H. Pryde, L. H. Princen & K. D. Mukherjee, Eds., Amer. Oil Chemists' Soc., Champaign, IL 1981, Chapter 21, p. 297.

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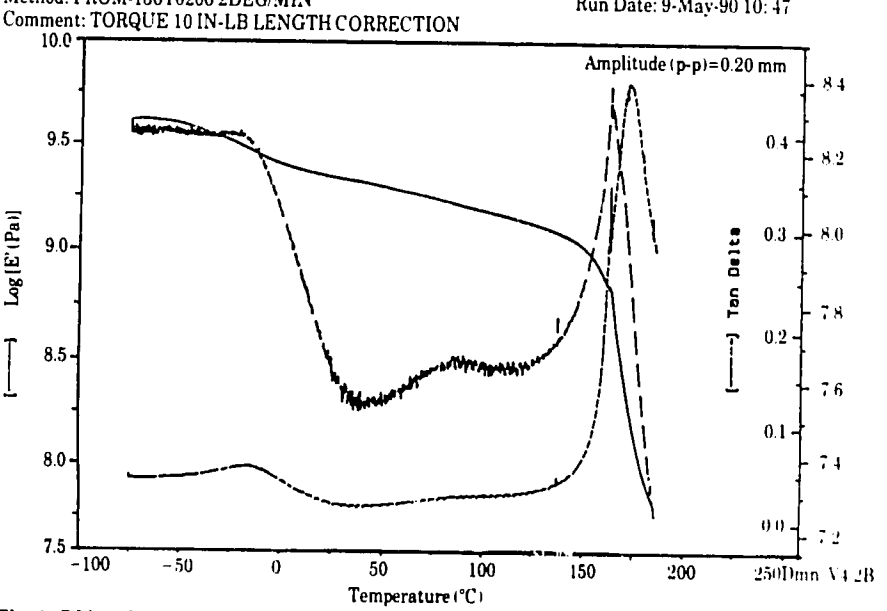

Fig 4: *DMA of two-phase epoxy resin: matrix based on Epon 825 and DDM (Tg = 160°C) and rubbery particles (20%) of vernonia oil and dodecanediamine (Tg = −22°C)*

9. F. Jones and S. Dirlikov, Fuels Derived from Vegetable Oils and Animal Fats; Process for Production of Same, Eastern Michigan University Patent Disclosure, October 1990.

RESEARCH CORPORATION TECHNOLOGIES
Invention Disclosure Form

I. Description

Please provide a title for your invention and a brief description. Inventions include new processes, products, apparatus, compositions of matter, living organisms—OR improvements to (or new uses for) things that already exist. Use additional sheets and attach descriptive materials to expand answers to questions. (Sketches, drawings, photos, reports and manuscripts will be helpful.)

A. Invention Title Fuels Derived from Vegetable Oils and Animal Fats; Process for Production of Same

B. Description Fuel is (1) a solution of partially or fully esterified or etherified glycerol in a fatty acid ester or (2) an emulsion of glycerol and, optionally, water in fatty acid ester. Four 1- and 2-step processes are visualized. Details are attached.

C. What are the immediate and/or future applications of the invention?

Liquid fuel. Probably best suited as diesel fuel. Could be blended with petrochemical fuel.

D. Why is the invention better—more advantageous—than present technology? What are its novel and unusual features? What problems does it solve?

Feasibility of using fatty acid esters as diesel fuel is established. A problem is cost of removal and disposal of by-product glycerol. Present invention overcomes problem by leaving glycerol in, using it as part of fuel. Also provides a way to use methanol (5.3¢ per pound) in diesel fuel.

E. Is work on the invention continuing? Are there limitations to be overcome or other tasks to be done prior to practical application? Are there any test data?

Initial process studies are planned. Plan to seek funding for detailed process study and testing in diesel engines.

F. Have products, apparatus or compositions, etc. actually been made and tested?

Solution of triacetin in methyl oleate shown to burn freely.

II. Publications, Public Use and Sale

Note: valid patent protection depends on accurate answers to the following items.

A. Has invention been disclosed in an abstract, paper, talk, news story or a thesis?

Type of disclosure None Disclosure Date _____

(Please enclose a copy)

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II. (Publications, Public Use and Sale—Continued)

B. Is a publication or other disclosure planned in the next six months?

Type of disclosure None Date _____
(Enclose drafts, abstracts, preprints)

C. Has there been any public use or sale of products embodying the invention?

Describe, giving dates No

D. Are you aware of related developments by others? If "yes," please give citations. Copies of any relevant patents or publications would be appreciated.

No, but have not searched literature.

III. Sponsorship

If the research that led to the invention was sponsored, please fill in the details and attach a copy of the contract or agreement if possible.

A. Government agency None contract/grant no. _____

B. Name of industry, university, foundation or other sponsor:

Coatings Research Institute, Eastern Michigan University

C. Has the invention been disclosed to industry representatives? If "yes," please provide details, including the names of companies and their representatives.

No. Parts of the concept were briefly discussed with Dr. Joe R. of the U.S. Department of Agriculture on September 24, 1990.

IV. For Our Records

A. Names and titles of inventors (please print; sign where indicated)

1. Frank N. Jones Signature Frank N. Jones Date 10/15/90
2. Stoil K. Dirlikov Signature Stoil Dirlikov Date 10/15/90
3. _____ Signature _____ Date _____

B. Contact for more data _____ Tel. ( )

C. Mailing address for inventor(s) _____

D. Name and title of institutional representative (please sign where indicated)

_____ Signature _____ Date _____

Department _____ Tel. ( )

Mailing address _____

RESEARCH CORPORATION TECHNOLOGIES
6840 East Broadway Boulevard
Tucson, Arizona 85710-2815

Telephone 602/296-6400

10/14/90

Estimated raw material cost of fuel

	$/lb	form. wt.
Palm or coco. oil	0.15	806 g/mol (assumed c.
Methanol	0.053	32
Acetic acid	0.29	60

Process, overall:

Oil	+	$HOCH_3$	+	CH_3COOH	−	H_2O	→	fuel
1 mol		3 mol		3 mol		3 mol		
806 g		96 g		180 g		54 g		1082 g

Cost / 1082 g	$
Oil	0.266
Methanol	0.011
Acetic acid	0.115
	0.392

Cost / lb = $1.645

Cost / gal = $1.24 (assuming sp gr = 0.9 g/mL

Possibilities for cost reduction

Use methanol -- make methyl ether / methyl ester
Partial acetylation
Use grease or lard -- 10 - 14¢/lb.

-FWJ

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MEMORANDUM OF INVENTION

FUELS DERIVED FROM VEGETABLE OILS AND FATS; PROCESSES FOR THEIR PRODUCTION

Revised October 4, 1990

OUTLINE OF REPRESENTATIVE CLAIMS -- HOMOGENEOUS FUELS

1. A homogeneous solution of (1) an ester of a fatty acid or of a mixture of fatty acids with (2) a derivative of glycerol selected from
   (a) ethers in which the fraction of OH groups etherified is sufficient to assure miscibility, and
   (b) esters in which the fraction of OH groups esterified is sufficient to assure miscibility.
   (c) optionally, a mixture of aliphatic and aromatic hydrocarbons; in this option the fraction of OH groups etherified or esterified is sufficient to assure miscibility of the entire system.
   (d) optionally, other additives such as detergents.

2. A homogeneous solution as in 1 having volatility suitable for use as fuel.

3. A homogeneous solution as in 1 having volatility suitable for use as diesel fuel.

4. A homogeneous solution as in 1a in which the derivative of glycerol is a partial ether of an aliphatic alcohol having 1 to 4 carbon atoms.

5. A homogeneous solution as in 1a in which the derivative of glycerol is a partial ether of a ethanol.

6. A homogeneous solution as in 1a in which the derivative of glycerol is a partial ether of methanol.

7. A homogeneous solution as in 1b in which the derivative of glycerol is a partial ester of an aliphatic carboxylic acid having 1 to 4 carbon atoms.

8. A homogeneous solution as in 1b in which the derivative of glycerol is a partial ester of acetic acid.

9. An internal combustion engine modified to enable it to operate with the homogeneous solution as in 1.

10. An automobile, truck, tractor, off-road vehicle, boat, aircraft or other vehicle modified to enable it to operate with the homogeneous solution as in 1. Modifications might include adjustments to the fuel injection system and temperature controllers on the fuel tank and delivery system.

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11. A fixed combustion device, such as a furnace, modified to enable it to operate with the homogeneous solution as in 1.

12. A process for preparation of the homogeneous solution of 1 in which a triglyceride (for example a vegetable oil or an animal fat) is (1) transesterified by reaction with an alcohol to form a mixture of fatty acid ester and glycerol, (2) the glycerol is partially etherified with an alcohol (the same or different) to form the homogeneous solution, and, optionally, (3) blended with aliphatic or aromatic hydrocarbons. Optionally, mixtures of alcohols may be used. In case of option (3), the etherification of step (2) is effected to an extent sufficient to render the final product homogeneous.

13. A process as in 12 in which the glycerol is not physically separated from the fatty acid ester after step (1), and the etherification of step (2) is effected in the presence of the fatty acid.

14. A process as in 13 in which step (1) is effected under basic or neutral conditions and step (2) is effected under acidic conditions.

15. A process as in 12, 13 and 14 in which the alcohol is ethanol.

16. A process as in 12, 13 and 14 in which the alcohol is methanol.

17. A process for preparation of the homogeneous solution of 1 in which a triglyceride (for example a vegetable oil or an animal fat) is (1) transesterified by reaction with an alcohol to form a mixture of fatty acid ester and glycerol, (2) the glycerol is partially or completely esterified with an aliphatic carboxylic acid with removal of by-product water to form the homogeneous solution, and, optionally, (3) blended with aliphatic or aromatic hydrocarbons. Optionally mixtures of alcohols and of acids may be used. In the case of option of (3), the esterification of step (2) is effected to an extent sufficient to render the final product homogeneous.

18. A process for preparation of the homogeneous solution of 1 in which a triglyceride (for example a vegetable oil or an animal fat) is (1) transesterified by reaction with an alcohol to form a mixture of fatty acid ester and glycerol, (2) the glycerol is partially esterified with an anhydride of an aliphatic carboxylic acid with removal of by-product aliphatic carboxylic acid to form the homogeneous solution, and, optionally, (3) blended with aliphatic or aromatic hydrocarbons. In the case of option of (3), the esterification of step (2) is effected to an extent sufficient to render the final product homogeneous.

19. Prccesses as in 17 and 18 in which the glycerol is not physically separated from the fatty acid ester before esterification.

20. A process as in 18 in which the mixture of fatty acid esters and glycerol from step (1) is, in step (2), reacted with acetic anhydride under substantially anhydrous conditions to esterify the mixture to a sufficient degree that a homogeneous solution is formed. By-product acetic acid may be removed by volatilization and recycled. Optionally, by-product acetic acid and other immiscible by-products, if formed, can be removed by water extraction.

21. A process for preparation of the homogeneous solution of 1 in which a triglyceride (for example a vegetable oil or an animal fat) is transesterified by reaction with an ester or a mixture of esters, preferably esters of a mono-alcohol and a monocarboxylic acid, optionally using a suitable catalysts such as litharge. Such a process would be essentially free of by-products. Optionally an excess of ester could be used.

22. The process of #21 in which the ester is selected from methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate and ethyl butyrate.

23. The process of #21 in which the ester or mixture of esters is, itself, suitable for use as a fuel, for example as diesel fuel; this will eliminate the possible need to remove excess ester after the reaction.

* * * * *

CLAIMS TO HETEROGENEOUS FUELS

1. An emulsion of glycerol in an ester of a fatty acid. Optionally the emulsion may be blended with liquid aromatic or aliphatic hydrocarbons. Optionally up to 10 wt. % water may be included in the emulsion to help stabilize the emulsion and to facilitate combustion.

2. An emulsion as in 1 in stabilized by a surfactant.

3. An emulsion as in 1 in which the surfactant is an aliphatic monoalcohol having 6 to 24 carbon atoms.

4. An emulsion as in 1 in which the surfactant is the monoglyceride of a fatty acid.

5. An emulsion as in 1-4 with volatility suitable for use as a fuel.

6. An emulsion as in 1-4 with volatility suitable for use as a diesel fuel.

7. An internal combustion engine modified to enable it to operate with the emulsion as in 5,6.

8. An automobile, truck, tractor, off-road vehicle, boat, aircraft or other vehicle modified to enable it to operate with the emulsion as in 5,6. Such modifications might, for example, consist of thermostatically controlled, agitated fuel tanks.

9. A fixed combustion device, such as a furnace, modified to enable it to operate with the emulsion as in 5,6.

10. A process for making the emulsions of 2, 3 and 4, in which a triglyceride is (1) transesterified by reaction with an aliphatic alcohol and (2) a surfactant is added and the mixture is subjected to physical mixing, and, optionally (3) the emulsion is blended with aliphatic or aromatic hydrocarbons, such as diesel fuel.

11. An emulsion as in 1-4 in which the alcohol used to esterify the fatty acid is selected from ethanol and methanol.

inv9-90

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TOUGHENING OF EPOXY RESINS BY EPOXIDIZED SOYBEAN OIL

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5'0

ABSTRACT

Homogeneous mixtures of a liquid rubber based on prepolymers of epoxidized soybean oil with amines, diglycidyl ether of bisphenol A epoxy resins, and commercial diamines form, under certain conditions, two-phase thermosetting materials which consist of a rigid epoxy matrix and randomly distributed small soybean rubbery particles. Particle size varies in the range from 0.1 to 5 microns and depends on the soybean fraction, degree of rubber prepolymerization, nature of diamine, kinetics of curing, etc.. Phase inversion phenomenon is observed at about 30% "soybean" content. Initial unoptimized results show that these two-phase thermosets have better toughness, similar to that of other rubber-modified epoxies, lower water absorption, and low sodium content. They exhibit slightly lower glass transition temperatures and Young's modili in comparison to the unmodified thermosets whereas their dielectric properties do not change. The epoxidized soybean oil is available at a price below that of commercial epoxy resins and appears very attractive for epoxy toughening in industrial scale.

1. INTRODUCTION

The toughening of epoxy resins by an elastomeric second phase was first demonstrated by McGarry et al. (1,2). It is now well established that a small amount of discrete rubbery particles with an average size of several microns, randomly distributed in a glassy, brittle epoxy thermoset, dissipates part of the impact energy, thus improving crack and impact resistance without major deterioration of other properties of the unmodified

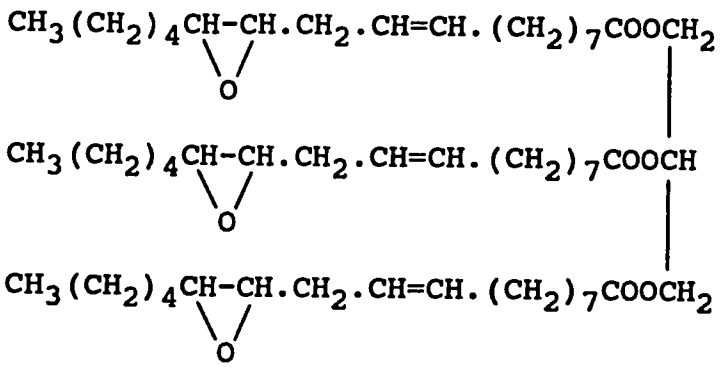
epoxy thermosets (3,4). The main role of the rubber phase in toughened epoxies is to relieve the constraints in the matrix through the principal mechanisms of cavitation and formation of shear bands (5,6). This phenomenon is used for toughening of epoxy resins in industrial scale.

The epoxy toughness is usually achieved by separation of a rubbery phase with a unimodal size distribution from the matrix during the curing process. Different reactive liquid rubbers, based on low molecular carboxy- or amino-terminated oligomers of butadiene and acrylonitrile (CTBN and ATBN), are usually used for the formation of the rubbery phase. Low molecular weight amino-terminated (methyl)siloxanes offer other alternatives. However, some of these oligomers are quite expensive.

Epoxidized vegetable oils such as vernonia, epoxidized soybean (ESO), and linseed oils (ELO) open new opportunities. Their epoxy resins with commercial diamines are elastomers at room temperature with low glass transition temperatures in the range of -70°C to 0°C, depending on the nature of the amine used for their curing.

Epoxidized vegetable oils, however, characterize by good compatibility and are known to be good polymer plasticizers. It appears unlikely that they form a second phase with epoxy resins. First, Sperling et al. (7) observed small scale heterogeneity in epoxy thermosets containing epoxidized vegetable oils. The broadening of the glass transition region in dynamic mechanical analysis (DMA) with the appearance of small additional loss peaks indicates that these formulations form semi-miscible thermosets.

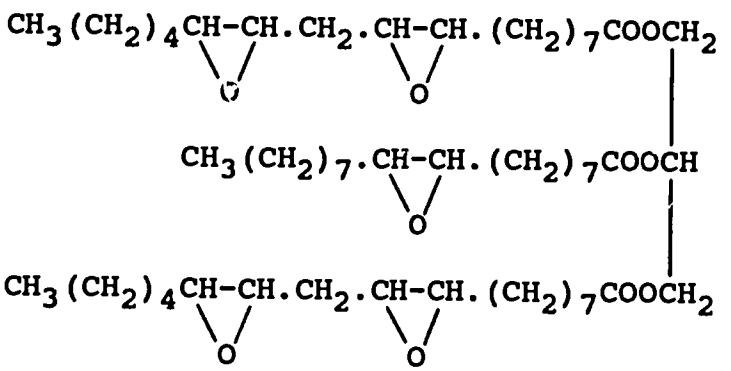
In our previous paper (8), we have described our initial results on toughening of epoxy thermosets with vernonia oil, a natural epoxidized vegetable oil, containing three epoxy rings and three carbon-carbon double bonds:



We have been able to obtain two-phase thermosets which consist of a rigid matrix of commercial epoxy resin with randomly distributed small "vernonia" rubbery, spherical particles. The vernonia particles separate during the curing process from the initial homogeneous mixture of epoxy resin (EPON 825), diamine: 4,4'-diaminodiphenylmethane (DDM) or 4,4'-diaminodiphenyl sulfone (DDS), and vernonia liquid rubber which is a B-staged material (soluble prepolymer) of vernonia oil with DDM or 1,12-dodecanediamine.

Although vernonia oil is at a developmental stage, it is still not available for industrial applications. We, therefore are evaluating other epoxidized vegetable oils for toughening of epoxy resins. The industrially produced epoxidized soybean and linseed oils are available at a low price, in the range of $0.50 to $0.65 per pound, and appear very attractive in this respect. In this paper, our initial unoptimized results on toughening of commercial epoxy resins by epoxidized soybean oil are described.

Epoxidized soybean oil consists of a mixture of different triglycerides. Their structures are schematically illustrated with the following formula:



2. EXPERIMENTAL

2.1 Materials

The epoxidized soybean oil is from Union Carbide Corporation produced under the commercial name Flexol^R Plasticizer EPO. The average epoxy functionality of this oil is approximately 4.5. Solid diglycidyl ether of bisphenol A (DGEBA), EPON 825 epoxy resin is a Shell Chemical Company product. All amine curing agents were purchased from Aldrich Chemical Co..

2.2 Epoxidized Soybean Liquid Rubber (ESR)

The epoxidized soybean liquid rubber was prepared by B-staging (prepolymerization) of epoxidized soybean oil with a stoichiometric amount of DDM. For this purpose, a mixture of 100 g of epoxidized soybean oil and 22.28 g of DDM was heated under nitrogen at 135°C for 37 to 40 hours until a highly viscous liquid was obtained which was still soluble in the commercial DGEBA epoxy resin at 70°C. The B-staging time varied slightly

from batch to batch depending on the quality of the epoxidized soybean oil used.

ESR density (1.05 g/cm^3 at 20°C) was determined with a pycnometer.

2.3 Cure Procedure

The epoxy formulations are based on stoichiometric mixtures of DGEBA and amine curing agent (DDM, DDS, etc.) containing 10, 15, 20, and 30 weight percent of epoxidized soybean liquid rubber or a stoichiometric mixture of the initial epoxidized soybean oil and amine curing agent. Their cure was carried out according to the following procedure: First, the mixture of DGEBA and epoxidized soybean oil or rubber was heated at 75°C under vacuum with stirring for 15-30 minutes. Then, the stoichiometric amount of the diamine (DDS, DDM, etc.) was added while stirring. The mixture was again degassed and stirred under a vacuum for an additional 15 min. at 150°C for the DDS formulations, or for 30 min. at 75°C for the DDM formulations. Then, it was poured into a mold which was preheated at 150°C for DDS and at 75°C for DDM formulations and again vacuumed for 15 min.. The final cure was carried out in an air-circulating oven at 150°C for 2 hours for the DDS formulations. DDM formulations were cured first at 75°C for 4 hours and then at 150°C for 2 hours.

2.4 Morphology

The morphology of the two-phase epoxy resins was studied by scanning electron microscopy (SEM) of the fracture surfaces using an Amray electron microscope, model 1000B.

2.5 Fracture Toughness

Single-edge-notched (SEN) specimens with approximate dimensions of 100 mm long x 12.7 mm width x 6.7 mm thick (Figure 1) were machined from castings. A sharp crack was introduced into the specimen by the strike of a razor blade, previously chilled in liquid nitrogen, with a rubber mallet. The tests were carried out with a three-point bending assembly, which was monitored by a servohydraulic materials testing machine (Instron 1331) with a span of 50.8 mm and a piston rate of 2.54 mm/s. A computer interface controled the machine and recorded the data. An HP model 310 computer was programmed to calculate the critical stress intensity factor, K_{IC}, using the following relation (9):

$$K_{IC} = Y \frac{2\ P\ S \sqrt{a}}{3\ t\ w^2}$$

where: P is the critical load for crack propagation in N,

S is the length of the span in mm,

a is the crack length in mm,

w is the width in mm,

t is the thickness in mm,

Y is the non-dimensional shape factor given by:

$$Y = 1.9 - 3.07\ (a/w) + 14.53\ (a/w)^2 - 25.11\ (a/w)^3 + 25.80\ (a/w)^4$$

The following simple relationship, which holds in our case of Linear-Elastic-Fracture Mechanics (LEFM) under plane strain conditions, was used for determination of the fracture energy,

G_{IC}:

$$G_{IC} = \frac{(1 - \nu^2)(K_{IC})^2}{E}$$

where ν is the Poisson ratio and E is the elastic or Young's modulus. At least 8 specimens of each formulation were used for determination of average fracture energy G_{IC}.

2.6 Uniaxial Tensile Test

Dog bone bars with dimensions of 6" x 0.5" x 1/8" (152mm x 12.7mm x 3.5mm) were cut with a high speed router and their external surface polished with very fine aliminium oxide sandpaper 220 (3M). A screw-driven Instron (model 1185), equipped with an extensometer for determination of the longitudinal strain and a computer interface type 4500 series, was used at a stroke of 60 mm/min.. At least ten specimens of each formulation were used for determination of their average tensile properties at room temperature.

2.7 Dynamic Mechanical Analysis (DMA)

A DuPont Thermal Analyzer 2100 instrument with DMA model 983, based on a flexural bending deformation measurement, and rectangular bar specimens with approximate dimensions of 45mm x 7.8mm x 3.5mm were used to study the dynamic mechanical properties over the temperature range from -130° to 200°C at a heating rate of 2°C/min..

2.8 Differential Scanning Calorimetry (DSC)

DSC measurements were carried out on DuPont Thermal Analyzer

2100 instrument with DSC model 2910.

2.9 Water Absorption

Maximum water absorption was determined on rectangular specimens with approximate dimensions of 45mm x 7.8mm x 3.5mm which were predried in a vacuum oven at 60°C to constant weight and then kept in boiling water for 3 to 4 weeks until saturation (e.g. to constant weight).

2.10 Dielectric Properties

Dielectric constant and dissipation factor were measured at 1 MHz and room temperature on specimens with 3" x 3" x 1/8" dimensions on a Genrad 1687 B Digibridge equipped with an LD-3 cell and by using the two-fluid method (air and DC-200, 1 cs).

2.11 Gel Permeation Chromatography (GPC)

GPC was measured on a Hewlett-Packard GPC instrument with Waters Associates differential refractometer model R401 and Polymer Laboratory gel columns.

2.12 Infrared Spectroscopy

Infrared spectra were taken by IBM Infrared Spectrometer 44.

2.13 Sodium Content

The epoxidized soybean oil and rubber samples were first dissolved by acid digestion. Their sodium content was determined with Perkin-Elmer 2380 Atomic Absorption Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Morphology

The morphology of the two-phase DGEBA/soybean epoxy thermosets was evaluated by scanning electron microscopy as an average of several micrographs taken at different fracture surfaces for each formulation. Our primary interest was in elucidation of the evolution process of the second (liquid or rubbery) phase and particle size determination. We, therefore, studied the morphology dependence on the weight percentage of "soybean" fraction and on the compatibility of the formulations: polarity of the diamine curing agent, degree of B-staging of the epoxidized soybean oil, etc..

The commercial epoxy resin used in the present study is EPON 825 which is practically pure DGEBA. Most of the research has been done with its stoichiometric DDM or DDS formulations. Only initial screening evaluation has been carried out on DGEBA formulations with other cycloaliphatic (isophorone diamine) and aliphatic diamines and polyamines (1,10-decanediamine, 1,12-dodecanediamine, diethylenetriamine, triethylenetetramine, etc.). These epoxy/amine formulations were toughened by the addition of 10, 15, 20 and 30 percent of epoxidized soybean oil or liquid rubber (prepolymer) as described in the experimental part.

Our initial attempts for toughening of epoxy resins were carried out directly with epoxidized soybean oil. For this purpose, homogeneous mixtures of DGEBA and diamine (DDM, isophorone diamine, different aliphatic di- and polyamines, etc.), containing 10 to 30 percent epoxidized soybean oil, were

cured according to a "standard" curing procedure for epoxy resin at 70°C. The diamines have a much higher reactivity with DGEBA than with the epoxy groups of the epoxidized soybean oil. As a result, they form a rigid matrix at 70°C in which the epoxidized soybean oil separates as a second phase of small liquid droplets. The electromicrograph of such a thermoset based on DGEBA, isophorone diamine and 20% epoxidized soybean oil shows a rigid matrix with random distribution of liquid "soybean" droplets with a diameter in the range of 1 micron (Figure 2). Unfortunately, at a higher temperature of 150°C these liquid droplets do not cure with the remaining diamine fast enough to form rubbery particles and we have not been able to prepare two-phase thermosets. Instead, soybean oil dissolves and plasticizes the rigid DGEBA matrix. One phase homogeneous thermosets with single lower glass transition temperatures are obtained as observed in SEM and DSC, respectively.

The toughening of the corresponding more polar (less miscible) DDS formulations directly by epoxidized soybean oil is under investigation. Similar DGEBA/DDS formulations toughened by vernonia oil undergo (macroscopic) phase separation at 150°C.

We were able to obtain two-phase thermosets with rubbery "soybean" particles under the same curing conditions by using epoxidized soybean liquid rubber (ESR) instead of the initial pure epoxidized soybean oil. These liquid rubbers were prepared by B-staging (prepolymerization) of a stoichiometric mixture of epoxidized soybean oil and DDM at 135°C for about 40 hours as described in the experimental section. A typical gel permeation chromatogram (GPC) of these soybean liquid rubbers is given in

Figure 3. They contain oligomers with a broad molecular weight distribution in addition to the unreacted initial epoxidized soybean oil which appears as a sharp peak at about 25 mins.

The "soybean" particles again separated from the initial homogeneous mixture of DGEBA, diamine and soybean liquid rubber. The higher molecular weight of soybean liquid rubber (in comparison to that of the soybean oil) increases its incompatibility with the epoxy matrix at higher temperature. As a result, the final thermoset, after being cured at 150°C, consists of a rigid epoxy matrix with randomly distributed small rubbery soybean spherical particles (Figure 4-10). The diamine molecules on the interface are expected to react with both the epoxy groups of the commercial epoxy resin and the unreacted epoxy groups of the epoxidized soybean rubber, and to form chemical bonds between the rigid matrix and the rubbery particles.

A plastification phenomenon at 150°C, similar to that described above for the pure epoxidized soybean oil, occurred under one-stage curing conditions for certain formulations based on soybean liquid rubbers as well. This was observed for formulations whose epoxy matrix and "soybean" rubbery phase had similar solubility parameters. Such formulations are based on less polar diamines as DDM; for example, the formulations based on DGEBA, DDM, and epoxidized soybean liquid rubber which are abbreviated here as DGEBA/DDM/ESR. Complete miscibility and homogeneous one-phase thermosets are obtained for these formulations at any soybean liquid rubber content if their one-

stage curing is carried out directly at higher temperatures, as for instance at 150°C. Under these conditions, the remaining epoxy groups of the soybean liquid rubber have higher reactivity and probably copolymerize with DGEBA without phase separation.

We have avoided the plastification of the DGEBA/DDM/ESR formulations and have prepared their two-phase final thermosets, which contain 15, 20 and 30% soybean liquid rubber (DGEBA/DDM/ESR-15, DGEBA/DDM/ESR-20, and DGEBA/DDM/ESR-30), by a two-stage curing procedure (see experimental section). The curing is carried out first at a lower temperature (70°C) at which the soybean epoxy groups have very low reactivity as their curing requires higher temperatures. At 70°C practically only DGEBA reacts with the diamine with the formation of free hydroxyl groups which increases its polarity. DGEBA also gradually increases its molecular weight and builds the rigid crosslinked matrix at 70°C. DGEBA higher molecular weight, crosslinking, and increased polarity result in higher incompatibility with the less polar hydrophobic epoxidized soybean liquid rubber which separates into small rubbery particles at this stage. Then, during the second curing stage, the temperature is increased to 150°C at which the less reactive soybean epoxy groups cure with the remaining diamine and form rubbery particles. Simultaneously, the matrix post-cures. Thus, the two-stage curing procedure allows kinetically to achieve the thermodynamic equilibrium (phase separation).

The formulations containing only 10% of soybean liquid rubber (DGEBA/DDM/ESR-10) however, produce a completely transparent one-phase material even following the two-stage

curing procedure. Obviously, only plastification of the DGEBA epoxy rigid matrix without phase separation occurs at low concentration of the soybean liquid rubber and we have not been able to obtain two-phase thermosets in this case. The solubility of the soybean liquid rubber in the DGEBA/DDM resin, however, is limited. The formulations with 10% soybean rubber are closed to saturation and we observe phase separation at slightly higher soybean content (15%).

Comparison of the DGEBA/DDM formulations toughened by epoxidized soybean oil (ESO) and rubber (ESR) at 10% level shows that DGEBA/DDM/ESO-10 forms a two-phase thermoset with small liquid soybean oil droplets at 70°C. However, they dissolve in the DGEBA/DDM matrix and form a homogeneous thermoset at 150°C. In contrast, DGEBA/DDM/ESR-10 formulation does not phase separate but forms a homogeneous casting at both temperatures: 70°C and 150°C. The epoxidized soybean rubber is more polar then the epoxidized soybean oil due to its free hydroxyl and amine groups and obviously it has better solubility in the DGEBA/DDM matrix at 70°C despite its higher molecular weight.

This plastification phenomenon was not observed for formulations based on more polar diamines than DDM, for instance those based on DDS. In these formulations abbreviated analogously, DGEBA/DDS/ESR, the solubility parameters of the "polar" epoxy matrix and "non-polar" soybean phase were quite different and the phase separation occurred at a lower conversion. DDS based formulations, therefore, do not require a two-stage curing procedure in order to build the molecular weight

of the matrix at lower temperature and increase the incompatibility between DGEBA and soybean phases. They form two-phase thermosets directly in one-stage curing procedure at a high temperature (150°C) (see experimental section).

Several factors control phase separation. Miscibility of the initial formulation of epoxy resin, amine, and epoxidized soybean oil or its liquid rubber is required. Incompatibility and phase separation should start during the curing process before gelation for spherical morphology formation. Simultaneously, the viscosity at this stage and the rate of cure should be high enough to prevent coalescence and macroscopic phase separation. The effective rubbery phase depends on the volume fraction of epoxidized soybean rubber, degree of its B-staging, nature (polarity, reactivity, molecular weight, etc.) of the epoxy resin and curing amine, and time and temperature of curing regime (kinetic factor).

The introduction of the epoxidized soybean liquid rubber into the DGEBA epoxy resin has obvious advantages for preparation of two-phase thermosets over the pure epoxidized soybean oil. The soybean liquid rubber has been prepared by B-staging (prepolymerization) of the epoxidized soybean oil with DDM (at 135°C for about 40 hours) under conditions at which an advanced degree of B-staging is achieved and the conversion is just "below" the gel point. Therefore, it requires a very short time at 150°C to reach its gel point and crosslink. Once cross-linked, the soybean liquid rubber is not able to dissolve into the matrix. Obviously, the "monomeric" epoxidized soybean oil requires a much longer time under the same conditions to reach

the "same" gel point. Thus, the lower level of matrix plastification in the presence of soybean liquid rubber, in comparison to the soybean oil, is probably due to two factors: its higher molecular weight and incompatibility at higher temperature (thermodynamic factor) and rapid crosslinking at 150°C (kinetic factor).

As mentioned earlier, the epoxidized soybean oil is a heterogeneous mixture of liquid oligomers and it contains a certain amount of the unreacted starting epoxidized soybean oil (Figure 3). No doubt, the latter has stronger plastification effect on the matrix than the higher molecular weight oligomers of ESR.

3.2 Particle Size

The average particle size of the rubbery soybean phase was determined by scanning electron microscopy simultaneously with the morphology as described in part 3.1. The average range of particle size distribution for the DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations is given in Table 1. Both the minimum and the maximum values are listed.

As mentioned above, DGEBA/DDM/ESR formulations with 10% content of soybean liquid rubber form homogeneous castings without separation of a second rubbery phase. The particle size of the DGEBA/DDM/ESR formulations with 15 and 20% soybean liquid rubber is in the range from 0.1 to 0.5 microns and it increases slightly to 0.8 microns at 30% rubber content (Table 1, Figure 4-6). DDM thermosets at any "soybean" rubber content characterize with an unimodal particle size distribution.

The DGEBA/DDS/ESR formulations with 10% soybean liquid rubber form two-phase thermosets with particle size of about 1-2 microns (Table 1). With 20% soybean rubber, the particle size increases ranging from 1 to 5 microns. These two formulations: DGEBA/DDS/ESR-10 and DGEBA/DDS/ESR-20 characterize with relative unimodal size distribution as well (Figure 7-8).

The average particle size and unimodal distribution in both types of formulations, DGEBA/DDM/ESR and DGEBA/DDS/ESR, are quite reproducible with the exception of the DGEBA/DDS/ESR-30 at a higher 30% soybean content. SEM micrographs show that the average size, range, and mode of distribution of the rubbery particles in this DGEBA/DDS/ESR-30 formulation are not reproducible and vary from specimen to specimen. Some specimens, for instance those used for tensile measurements, characterize with a very broad unimodal distribution with particle size ranging from 1 to 17 microns (Table 1, Figure 9). A bimodal particle distribution, however, is often observed for this formulation as well. For example, the specimens, used for determination of fracture toughness, show a bimodal size distribution with smaller particles in the range of 5 to 10 microns and larger particles in the range of 100 to 200 microns (Table 1, Figure 10). SEM micrographs of the formulations with such bimodal particle distribution show that not only are the average size and range of the particles not reproducible, but also the apparent volume fraction varies from specimen to specimen without change in the overall morphology. As a matter of fact, the apparent volume fraction of the rubbery phase, observed

on the SEM micrographs of the DGEBA/DDS/ESR-30 formulations with both unimodal and bimodal particle size distribution, is greater than the actual volume soybean fraction. It indicates, first, that the larger particles in the DGEBA/DDS/ESR-30 formulations with bimodal distribution are a result of occlusion of DGEBA epoxy component into the soybean rubbery particles and second, on close proximity to the phase inversion point at 30% soybean rubber. Such phase inversion phenomena have been observed by Lee et al. (10) for a similar formulation: DGEBA/DDS/CTBN at a high 30% CTBN liquid rubber content.

Recently, we were able to confirm experimentally the phase inversion phenomena and the occlusion of DGEBA resin in the rubbery particles in a similar formulation: DGEBA/DDM/vernonia rubber at 20% vernonia rubber by SEM micrographs of specimens treated with osmium tetraoxide (unpublished data). Vernonia oil contains carbon-carbon double bonds in contrast to the epoxidized soybean oil. It stains with osmium tetraoxide and its rubbery phase is easily distinguished from the DGEBA resin in SEM micrographs.

The miscibility and phase separation in close proximity to the phase inversion point depends highly on the kinetic factors. A small deviation in temperature and/or time of the curing process causes a shift in the phase inversion point, broad variation of morphology observed for different specimens, and fluctuation of their physico-mechanical properties, as discussed later in part 3.4 and 3.5.

It is not clear, however, why DGEBA/DDS/ESR-30 results in bimodal distribution (in some specimens) and appears to be close

to the phase inversion point, whereas the corresponding DGEBA/DDM/ESR-30 with the same soybean rubber content do not exhibit these phenomena. It is probably due to two factors:

First, different procedures were used for the curing of the DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations. The DGEBA/DDS/ESR-30 formulation was cured directly for 2 hours at 150°C. The DGEBA/DDM/ESR-30 was cured according to a two-stage curing procedure: first at 75°C for 4 hours and then at 150°C for 2 hours. As discussed above, the two-stage procedure allows the matrix formation at a lower temperature and results in better separation of the soybean rubber (perhaps without DGEBA occlusion). Direct comparison of the morphology and rubbery particle size and distribution of DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations, however, both prepared under the same curing conditions, is difficult. DDS has a high mp = 177°C and requires a higher temperature (above 130°C) to dissolve in the initial DGEBA/ESR formulation and form homogeneous mixtures. Its DGEBA/DDS/ESR formulations, therefore, can not be cured by the two-stage procedure. They were cured in one-stage directly at a higher temperature (150°C). In contrast, DDM has a lower mp = 91°C and its starting DGEBA/DDM/ESR formulations are homogeneous mixtures at much lower temperature. DDM formulations, however, are more compatible and they form only one-phase thermosets without phase separation by the direct one-stage curing procedure at a high temperature (150°C).

Second, the formation of larger rubbery particles and DGEBA occlusion at the phase inversion point depend on the mutual

miscibility of DGEBA resin and soybean rubber and especially on the solubility partition constants of the DGEBA monomer in the matrix and in the rubbery phase at different stages of curing. The DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations characterize with different miscibility. At an earlier stage of curing, the initial unreacted (non-polar) DGEBA monomer of the DGEBA/DDS/ESR formulations, especially those with a higher ESR content, has a relatively higher solubility in the non-polar ESR rubber phase than in the highly polar DDS dominated DGEBA/DDS "matrix" phase which characterizes with strong hydrogen bondings between amine, hydroxyl, and sulfone groups. (As a matter of fact, DGEBA monomer is miscible at any ratio at room or elevated (70°) temperature with the epoxidized soybean rubber but it is completely insoluble in DDS). The DGEBA monomer, dissolved in the rubbery phase, reacts with the diamine with the progressing cure time and phase separates at a later stage with the formation of small rigid particles within the large rubbery particles. Therefore, we observe much larger particles (100-200 microns), greater apparent rubbery volume fraction (than the actual "soybean" volume fraction) and phase inversion phenomenon at a relatively lower soybean content (at about 30%) for the DGEBA/DDS/ESR formulations. In contrast, the DGEBA monomer of the DGEBA/DDM/ESR formulations has relative lower solubility under the same conditions in the rubbery phase since the DGEBA/DDM "matrix" phase is much less polar than the DGEBA/DDS phase. As a matter of fact, DGEBA monomer is miscible with DDM at a much lower temperature. As a result, the rubbery particles of the DGEBA/DDM/ESR-30 formulation do not contain smaller rigid DGEBA

particles even at 30% soybean rubber and their apparent volume fraction corresponds to the actual "soybean" content. The formation of larger particles and phase inversion phenomenon for the DDM formulations is expected to occur at a higher soybean content. Phase diagrams of both formulations and further SEM evaluation on the fracture surface of these thermosets are under investigation. Similar miscibility phenomena have been reported by Romanchick et al. (11) for CTBN modified DGEBA epoxy resins.

The SEM micrographs of all DDM and DDS based formulations with 10, 15, 20, and 30% soybean content display rough fracture surfaces. Evidently, the soybean rubbery particles cavitated under the shear (fracture) deformation with the formation of deep voids (Figure 4-9). A comparison of both formulations has shown more rough fracture surface and less pronounced cavitation phenomenon in the DGEBA/DDS/ESR formulations. Some of their particles are clearly observed in SEM. Only a part of them have cavitated with the formation of some deep voids. The cavitation process is much more efficient in the case of smaller rubbery particles of DGEBA/DDM/ESR formulations where complete cavitation and more smooth fracture surface are observed.

The results also show that DGEBA/DDS/ESR and DGEBA/DDM/ESR formulations characterize with different particle size at the same soybean rubber content (Table 1). It indicates that the particle size depends on the compatibility of the formulations.

The DGEBA/DDM/ESR formulations are expected to have better compatibility than the DGEBA/DDS/ESR formulations since both their DGEBA epoxy matrix and soybean rubber phase are based on

the same DDM diamine. In addition, DDM is less polar than DDS. The solubility parameter of the DDM matrix in the DGEBA/DDM/ESR formulations, therefore, matches the solubility parameter of the "non-polar" soybean liquid rubber much better than does the more polar DDS matrix in the DGEBA/DDS/ESR formulations. As a result of their better compatibility, the DGEBA/DDM/ESR formulations with a 10% soybean content form homogeneous thermosetting material without phase separation. The rubbery particles observed in the formulations with 15, 20, and 30% soybean rubber are formed at a later stage in curing and have a smaller diameter.

The DGEBA/DDS/ESR formulations are less compatible because first, they are based on two different diamines: DDS in the rigid matrix and DDM in the rubbery phase; and second, their DDS matrix is more polar (see above). The DGEBA/DDS/ESR formulations, therefore, characterize with bigger rubbery particles which separate at earlier stages of curing from the initial liquid homogeneous mixture. Their particle size increases much more rapidly with the increasing soybean rubbery content, especially in close proximity to the phase inversion point, due to DGEBA occlusion, than does the particle size of the DGEBA/DDM/ESR formulations (Table 1).

These results show that under the same curing conditions but using different diamines, one can easily vary the particle size of the rubbery phase in the range of the desirable particle size for toughening of epoxy thermosets, e.g. ranging from 0.1 to 10 microns. In general, larger particles (and even macroscopic total phase separation) were observed for less compatible

formulations with more polar diamines used for curing of the rigid matrix, for instance DDS. In addition, a lower viscosity of the formulations (at higher temperature) allows coalescence of the liquid soybean droplets and results in the formation of bigger rubbery particles. In contrast, higher curing rates result in rapid crosslinking, prevent coalescence, and thus produce smaller rubbery particles.

In summary, the particle size depends on the nature of the diamines used for curing the matrix and for preparation of the soybean liquid rubber, the volume fraction of the epoxidized soybean rubber, its degree of B-staging, viscosity of the formulations and rate of cure, e.g. temperature and time of B-staging and cure of the final thermoset (cure kinetics), etc..

3.3 Glass Transition Temperature (T_g)

The temperature dependence of the storage modulus and tan delta of the two "pure" matrices: DGEBA/DDM and DGEBA/DDS was determined by dynamic mechanical analysis in the temperature range of -130° to $+200^{o}C$ (Figure 11-14). Both thermosets were prepared without soybean rubber under the same curing conditions as the corresponding two-phase materials in the presence of soybean rubber.

The glass transition temperatures of these one-phase DGEBA/DDM and DGEBA/DDS thermosets were observed at 190° and $185^{o}C$ respectively. In addition, the DGEBA/DDM and DGEBA/DDS thermosets exhibited beta-relaxations at lower temperatures: -30° and $-35^{o}C$ respectively (Table 2).

We were not able to measure the DMA of the pure epoxidized

soybean rubber (ESR) cured under the same conditions in the absence of DGEBA/diamine component. Its glass transition temperature (T_g = -25°C) was determined by differential scanning calorimetry (Figure 15, Table 2). Obviously, this thermoset exists in a rubbery state at room temperature and appears to be suitable for toughening of commercial (brittle) epoxy resins.

The temperature dependence of the storage modulus and tan delta of both types of formulations: DGEBA/DDM/ESR and DGEBA/DDS/ESR at different contents of soybean liquid rubber was determined by DMA (Figure 12-15). All formulations exhibited two transitions at higher and lower temperatures (Table 2).

The higher temperature transitions of the DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations occur in close proximity to the glass transition temperature of the pure DGEBA/DDM and DGEBA/DDS thermosets: in the range of 145° to 190°C. Therefore, these transitions have been assigned to the glass transition temperatures of their DGEBA matrices. These glass transition temperatures gradually decrease in the corresponding DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations with an increasing amount of soybean liquid rubber. Obviously, a part of the soybean rubber, and especially its lower molecular weight oligomers and its unreacted epoxidized soybean oil, dissolves and plasticizes the DGEBA rigid matrix.

This plastification phenomenon is more pronounced for the DGEBA/DDM/ESR formulations. The depression of the glass transition temperature of their matrices is about 25°C at 15 to 20% of soybean rubber content, and almost 45°C at 30% loading.

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As discussed in part 3.2, the DGEBA matrix and soybean rubber characterize with better compatibility in the DDM formulations than in those based on DDS. It results in better plastification and high concentration of the soybean rubber in the DGEBA phase. This is confirmed here by greater depressions observed for the glass transition temperature of their matrices.

Smaller depressions of the glass transition temperature of the matrix are observed for the less compatible DGEBA/DDS/ESR formulations. Their T_g decrease from about 15°C at 10% soybean liquid rubber to approximately 25°C at 30% loading.

The lower temperature transitions of the DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations are observed in the range of -30°C to -45°C. There are no other detectable transitions for these formulations, either at a higher temperature in the range of -30° to +130°C or at a lower temperature in the range of -45° to -130°C. Therefore, we believe that the glass transition (temperature) of the ESR rubbery particles and the beta-transition of the matrix of the two-phase formulations overlap in the range of -30° to -45°C and are observed as a single transition at a lower temperature.

The glass transition temperature of the rubbery particles in the two-phase thermosets was expected to correspond to that of the pure ESR rubber or to appear at a slightly higher temperature if the rubbery particles dissolved a certain amount of DGEBA epoxy component which has a higher T_g. Surprisingly, the low transition temperatures of the two-phase thermosets are observed at a slightly lower temperature than the glass transition temperature of the pure ESR rubber. This discrepancy is probably

due to the different methods used for determination of these transitions: DMA is used for the two-phase thermosets and DSC for the pure ESR rubber. It might also result as an artifact from the overlapping of the glass transition of the rubbery particles and the beta-transition of the matrix or by stresses induced by thermal shrinkage as discussed by Gillham (12). The slight increase of the lower temperature transition observed for the DGEBA/DDS/ESR-30 formulation with bimodal particle size distribution could be attributed to the occlusion of epoxy resin into the larger rubbery particles. In any case, the glass transition temperature of the pure soybean rubber (ESR) does not change much in the presence of the DGEBA matrix in both DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations. It indicates that the rubber phase in these two-phase thermosets does not contain a significant amount of the DGEBA component below their phase inversion point and they are practically formed by pure soybean rubber.

3.4 Fracture Toughness

The fracture toughness, in terms of the stress intensity factor, K_{IC} and fracture energy, G_{IC}, is given in Table 3 for both formulations: DGEBA/DDM/ESR and DGEBA/DDS/ESR.

A better toughening effect, which gradually increases at a higher "soybean" content, is observed for the DGEBA/DDM/ESR formulations. It is probably due to the plastification phenomenon which occurs at a larger scale for these formulations (see part 3.2 and 3.3). The "soybean" component, which acts as a plasticizer of the matrix, improves its toughness. These

formulations also characterize with smaller particle size (Table I, 0.1-0.8 microns) and their fracture surface shows extensive particle cavitation and the formation of deep voids (see part 3.2, Figure 4-6). Pearson and Yee (J. Mater. Sci. 1990, in press) have shown that the toughening mechanism of elastomer modified epoxies is governed by the phenomena of internal cavitation of rubber particles and the formation of shear bands. The efficiency of these mechanisms depends on rubber particle size. They have demonstrated that smaller particles ranging from 0.2 to 2 microns are more efficient and produce a better toughening effect than larger particles. The higher values for fracture energy observed for the DGEBA/DDM/ESR formulations are probably due to both their better compatibility (plastification) and smaller particles (in the range from 0.1 to 0.8 microns, Table I) with more efficient toughening mechanism.

A smaller improvement of the fracture toughness is observed for the DGEBA/DDS/ESR formulations. Plastification plays a smaller role here and they characterize with larger rubbery particles. In agreement with Yee's results discussed above, their larger particles act as "bridging particles" with only a modest increase in fracture toughness. In addition, DGEBA/DDS/ESR formulations seem to exhibit an optimum of toughening at 20% "soybean" component. The DGEBA/DDS/ESR-30 specimens at 30% soybean liquid rubber, which were used here for determination of fracture toughness, characterize with bimodal particle size distribution and they are close to their phase inversion point (see part 3.2). Physico-mechanical properties of

epoxy resins start to deteriorate rapidly at the phase inversion point and we, therefore observe lower fracture toughness for the DGEBA/DDS/ESR-30 thermoset.

In summary, our measurements show that the introduction of soybean liquid rubber remarkably improves the fracture toughness of commercial highly crosslinked, brittle epoxy resins such as DGEBA/DDS and DGEBA/DDM, which exhibit low ductility and, as shown by other authors (13,14), are very difficult to toughen.

3.5 Tensile Properties

Young's moduli were determined from the corresponding tensile stress/strain curves. They are reported here as an average value of several independent tensile measurements in order to minimize the fluctuations observed in our tensile data as a result of the specimens' high stiffness (Table 4).

The dependence of Young's modulus on the soybean content is plotted in Figure 17 for both types of formulations DGEBA/DDM/ESR and DGEBA/DDS/ESR. As expected, the elastic moduli gradually decrease with the increasing soybean fraction. Linear relationships can approximately fit the different points for both formulations and a slight deviation is observed only with a higher content of soybean rubber. The slope of the DGEBA/DDS/ESR formulations, however, is steeper than that of DGEBA/DDM/ESR. Their tensile properties decrease faster with the increasing soybean content. This result may be attributed to the bigger rubbery particles of the DGEBA/DDS/ESR formulations.

Surprisingly, the linear tensile dependence of the DGEBA/DDS/ESR formulations on the soybean rubber content does not

correlate well with the corresponding fracture toughness relationship which shows an optimum at 20% and a drop in fracture toughness at 30% soybean content. As discussed in part 3.2, the DGEBA/DDS/ESR formulation at 30% soybean content is close to its phase inversion point and its different specimens have different morphology. Indeed, direct comparison of the SEM micrographs on the fracture surface of the DGEBA/DDS/ESR-30 formulation show that the tensile specimens, used in this study, characterize with a unimodal particle size distribution ranging from 1 to 17 microns (Table 1, Figure 9). In contrast, the specimens used for fracture toughness measurements show a bimodal distribution with smaller particles ranging from 5 to 10 microns and larger particles ranging from 100 to 200 microns (Table 1, Figure 10). The different morphology of the DGEBA/DDS/ESR-30 specimens used for tensile and fracture toughness measurements obviously result in fluctuation of their physico-mechanical properties.

3.6 Water Absorption

The high water absorption is another major disadvantage of the commercial epoxy resins in addition to their poor fracture toughness. The maximum water absorption of the DGEBA/DDS/ESR and DGEBA/DDM/ESR formulations was determined on their predried samples in boiling water to their constant weight as described in the experimental part. Although our results are somewhat lower than expected, the water absorption of both formulations DGEBA/DDM/ESR and DGEBA/DDS/ESR decreases gradually and linearly with the increasing soybean content (Table 5). Obviously, the highly hydrophobic long fatty chains of the epoxidized soybean

oil reduce the water absorption of its epoxy thermosets. As expected, the DGEBA/DDS/ESR formulations at different soybean liquid rubber contents have a higher water absorption than the corresponding DGEBA/DDM/ESR formulations, due to the more polar character of DDS in comparison to DDM.

3.7 Dielectric Properties

The dielectric constant and dissipation factor of the DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations are given in Table 6. The introduction of epoxidized soybean oil, with its long aliphatic chains, was expected to lower simultaneously the dielectric constant and dissipation factor of the commercial epoxy resins, despite the formation of free hydroxyl groups by the opening of its epoxy rings. Surprisingly, the dielectric properties of both types of formulations do not change (decrease) much with the increasing soybean liquid rubber content. Although we do not have an explanation for this observation at the present moment, Shimp (Rhone-Poulenc, personal communication, 1990) has suggested that, in addition to the traditional epoxy curing reaction, the epoxidized soybean oil (and rubber) might undergo amidolysis with the aromatic DDS or DDM diamines under our curing conditions, according to Scheme 1, with the formation of additional glycerol free hydroxyl groups and fatty acid amide groups, both with very high dielectric properties. These by-products will increase the dielectric constant and dissipation factor of their two-phase thermosets and balance the reducing effect of the long aliphatic chains of the epoxidized soybean oil.

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In order to prove that such amydolysis takes place, we measured consecutive infrared spectra of a stoichiometric mixture of epoxidized soybean oil and DDM with progressing B-staging time (Figure 17). B-staging (or prepolymerization) was carried out at 135°C for 48 hours under similar conditions, at which the castings, used for determination of the dielectric properties, were prepared. The infrared spectrum of the initial pure epoxidized soybean oil exhibit a single absorption band at about 1730 cm^{-1} which corresponds to the stretching >C=O vibrations of its carbonyl -COO groups. A comparison of this infrared spectrum to that of the B-staged materials with progressing B-staging time does not reveal any new absorption bands for the >C=O vibrations of the amide -COONH groups of the by-product or any other changes in the region of 1800-1650 cm^{-1}. It indicates that if the amydolysis reaction indeed proceeds simultaneously with the traditional epoxidation reaction, it does so only to a limited extend.

3.8 Sodium Content

A requirement for the application of epoxy resins in the electronics industry is their low ionic content, often below 10 ppm, especially for sodium and chlorine ions. Electronics-grade epoxy resins are significantly more expensive due to the additional purification procedure needed to lower their ionic content.

The epoxidized soybean oil and liquid rubber, without any purification, characterize with a very low content of sodium of 16.5 and 12.5 ppm respectively, and probably of other ionic

species. It is due to the hydrophobic non-polar molecular structure of the epoxidized soybean oil lacking free hydroxyl or carboxyl groups. Thus, epoxidized soybean rubber appears especially suitable for the toughening of epoxy resins for electronics applications.

3.9 Epoxidized Soybean Oil v.s. Vernonia Oil

In general, the morphology, particle size, toughening, etc. of DGEBA/DDM and DGEBA/DDS epoxy formulations modified by epoxidized soybean oil or rubber resemble those of the corresponding two-phase thermosets based on vernonia oil and rubber (8) prepared under similar conditions. A comparison of their effect also shows several differences. Although vernonia oil has a structure similar to that of the epoxidized soybean oil, it characterizes with a lower epoxy functionality. It contains an average of 2.4 epoxy groups per triglyceride molecule, e.g. only half of the average 4.5 epoxy groups of the epoxidized soybean oil. Vernonia oil and rubber, therefore, are expected to have less polar characters than the epoxidized soybean oil and rubber, lower compatibility with the commercial epoxy resins, and produce rubbery particles with lower crosslinking density. In good agreement, our results (8) show the formation of bigger "vernonia" particles whose separation proceeds at an earlier stage of B-staging and curing of "vernonia" formulations of commercial epoxy resins. For example, the DGEBA/DDM formulation containing 10% vernonia rubber forms two-phase thermosets whereas the corresponding DGEBA/DDM/ESR-10 is homogeneous. In addition, "vernonia" rubbery particles have a

lower glass transition temperature which reflects their lower crosslinked density.

These results show that one could vary the morphology, particle size, and presumably the fracture toughness (together with the other physico-mechanical properties) of the commercial epoxy resins not only by changing the nature and polarity of the diamine curing agent as discussed previously (see part 3.1-3.5), but also by variation of the nature and degree of epoxidation of the vegetable oils.

3.10 Epoxidized Vegetable Oils v.s. CTBN Liquid Rubber

It is also interesting to compare the effect of the epoxidized vegetable oils with that of CTBN liquid rubber which is commonly used for epoxy toughening presently. According to recent studies by Yee et al. (13) on the toughening of epoxy resins under similar conditions, the introduction of 10% CTBN liquid rubber into a DGEBA/DDS epoxy resin produces two-phase thermosets with CTBN rubbery particles with a diameter of about 5 microns. The fracture energy of the unmodified DGEBA/DDS thermoset increases from G_{IC} = 162 J/m^2 to G_{IC} = 242 J/m^2 in the presence of 10% CTBN, e.g. with ΔG_{IC} = 80 J/m^2, whereas its Young modulus simultaneously decreases from E = 3360 MPa to E = 3000 MPa (13). Our unmodified DGEBA/DDS thermoset exhibits similar fracture toughness (G_{IC} = 145 J/m^2) and Young's modulus (E = 3420 MPa) (Table III and IV) as those reported by Yee (13). The corresponding soybean modified DGEBA/DDS/ESR-10 thermoset at the same rubber content, however, has smaller rubbery particles ranging from 1 to 2 microns (Table I). The introduction of 10%

soybean liquid rubber more than doubles the fracture energy of the unmodified DGEBA/DDS thermoset from G_{IC} = 145 J/m^2 to G_{IC} = 374 J/m^2 (Table III), e.g. with ΔG_{IC} = 229 J/m^2, whereas the Young modulus decreases from E = 3420 MPa to a slightly lower value of E = 2810 MPa (Table IV) than that observed for the CTBN-modified thermoset by Yee et al. (13). Comparing the toughening effect at 10% content level, the soybean liquid rubber (ΔG_{IC} = 229 J/m^2) appears to be more effective than CTBN (ΔG_{IC} = 87 J/m^2).

Comparison of the SEM micrographs shows a relative smooth fracture surface for the DGEBA/DDS/CTBN-10 thermoset (13). In contrast, the corresponding soybean modified DGEBA/DDS/ESR-10 fracture surfaces show extensive deep voids and more pronounced particle cavitation. These phenomena are characteristic for smaller rubbery particles and result in a better toughening effect observed for the soybean liquid rubber.

Another advantage of the epoxidized soybean rubber is its low sodium content (12,5 ppm) in contrast to the higher sodium content of the carboxy-terminated CTBN (in the range of 300 ppm) (R. Drake, B. F. Goodrich, personal communication, 1991). Low ionic content is an important characteristic of the liquid rubbers used for the toughening of epoxy resins for electronics applications (see part 3.8). Reduction of the sodium content of CTBNs requires additional washing (purification).

Finally, epoxidized soybean oil is industrially produced and available at about 50 cents per pound, a price below that of CTBN (in the range of $2.00 - $2.50 per pound). It makes the toughening of commercial epoxy resins by epoxidized soybean oil

very attractive for commercial applications in large scale.

In summary, the epoxidized soybean oil appears to have three potential advantages over CTBN for the toughening of epoxy resins: better toughening effect, lower sodium content, and lower price.

4. CONCLUSION

Homogeneous mixtures of epoxidized soybean rubber (and probably rubber of any other epoxidized vegetable oil), commercial epoxy resins based on diglycidyl ether of bisphenol A (EPON 825, etc.), and commercial diamines (DDS, DDM, etc.) form, under certain conditions, two-phase thermosetting materials which consist of a rigid epoxy matrix and randomly distributed small rubbery particles of cured epoxidized soybean oil. Particle size varies ranging from 0.1 to 5 microns and depends on the nature of diamine, B-staging conditions, kinetics of curing, etc..

Although further research is required, our initial unoptimized results show that these two-phase thermosetting materials have better toughness, comparable (if not better) to that of the CTBN modified epoxies, lower water absorption, low sodium content, and they may even be more environmentally friendly. They exhibit slightly lower glass transition temperatures and Young's modili in comparison to the unmodified thermosets whereas their dielectric properties do not change. Optimization of the preparation conditions is expected to further improve their physico-mechanical properties.

Several options for epoxy toughening directly by epoxidized soybean oil, especially of DDS formulations are under

investigation. Epoxidized soybean oil is industrially produced and available at about 50 cents per pound, a price below the least expensive epoxy resins based on DGEBA ($1.25 - $1.35 per pound) and much lower than the price of CTBN (in the range of $2.00 - $2.50 per pound) which is commonly used for epoxy toughening presently. It makes the toughening of commercial epoxy resins by the epoxidized vegetable (soybean) oils and rubbers very attractive for commercial applications in large scale.

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Table I. Average range of "soybean" particle size distribution of the rubber modified DGEBA/DDM/ESR and DGEBA/DDS/ESR thermosets.

Thermoset Formulation	Particle size, microns
DGEBA/DDM/ESR-10	no phase separation
DGEBA/DDM/ESR-15	0.1-0.5
DGEBA/DDM/ESR-20	0.1-0.4
DGEBA/DDM/ESR-30	0.1-0.8
DGEBA/DDS/ESR-10	1-2
DGEBA/DDS/ESR-20	1-5
DGEBA/DDS/ESR-30[a]	1-17
DGEBA/DDS/ESR-30[b]	5-10, 100-200

[a]Tensile specimens, [b]Fracture toughness specimens.

Table II. DMA lower and higher temperature transitions of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations.

Thermoset Formulation	Transition, °C[a]	°C[b]
DGEBA/DDM	-30	190
DGEBA/DDM/ESR-15	-35	161
DGEBA/DDM/ESR-20	-33	165
DGEBA/DDM/ESR-30	-39	145
DGEBA/DDS	-35	185
DGEBA/DDS/ESR-10	-45	168
DGEBA/DDS/ESR-20	-43	166
DGEBA/DDS/ESR-30	-30	161
ESR[c]	-25	

[a]The lower transition temperature corresponds to an overlap in the glass transition temperature of the rubbery particles and beta-transition of the DGEBA matrix. [b]Glass transition temperature of the DGEBA matrix. [c]Determined by DSC.

Table III. Stress intensity factor, K_{IC} and fracture energy, G_{IC} of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations.

Thermoset Formulation	K_{IC}, $MPa.m^{1/2}$	G_{IC}, J/m^2
DGEBA/DDM	0.75	175
DGEBA/DDM/ESR-10[a]		
DGEBA/DDM/ESR-15	1.24	564
DGEBA/DDM/ESR-20	1.33	802
DGEBA/DDM/ESR-30	1.40	1008
DGEBA/DDS	0.75	145
DGEBA/DDS/ESR-10	1.09	374
DGEBA/DDS/ESR-20	1.19	596
DGEBA/DDS/ESR-30	0.54	145

[a]This formulation does not phase separate and its fracture toughness has not been determined.

Table IV. Young modulus, E of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations.

Thermoset Formulation	E, MPa
DGEBA/DDM	2840
DGEBA/DDM/ESR-10[a]	
DGEBA/DDM/ESR-15	2410
DGEBA/DDM/ESR-20	1950
DGEBA/DDM/ESR-30	1720
DGEBA/DDS	3420
DGEBA/DDS/ESR-10	2810
DGEBA/DDS/ESR-20	2100
DGEBA/DDS/ESR-30	1780

[a]This formulation does not phase separate and its tensile properties have been determined.

Table V. Maximum water absorption of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations.

Thermoset Formulation	Water Absorption, %
DGEBA/DDM	2.42
DGEBA/DDM/ESR-15	2.22
DGEBA/DDM/ESR-20	2.00
DGEBA/DDM/ESR-30	1.62
DGEBA/DDS	3.61
DGEBA/DDS/ESR-10	3.33
DGEBA/DDS/ESR-20	3.13
DGEBA/DDS/ESR-30	2.80

Table VI. Dielectrical properties of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations.

Thermoset Formulation	Dissipation Factor $\times 10^{-2}$	Dielectrical Constant
DGEBA/DDM	3.3	3.78
DGEBA/DDM/ESR-15	3.5	3.78
DGEBA/DDM/ESR-20	3.6	3.77
DGEBA/DDM/ESR-30	3.7	3.77
DGEBA/DDS	2.5	3.95
DGEBA/DDS/ESR-20	3.3	3.88

Scheme 1. Proposed amydolysis of epoxidized soybean oil with aromatic diamines ($NH_2.R.NH_2$) under the curing conditions (D. Shimp, Rhone-Poulenc, personal communication, 1990).

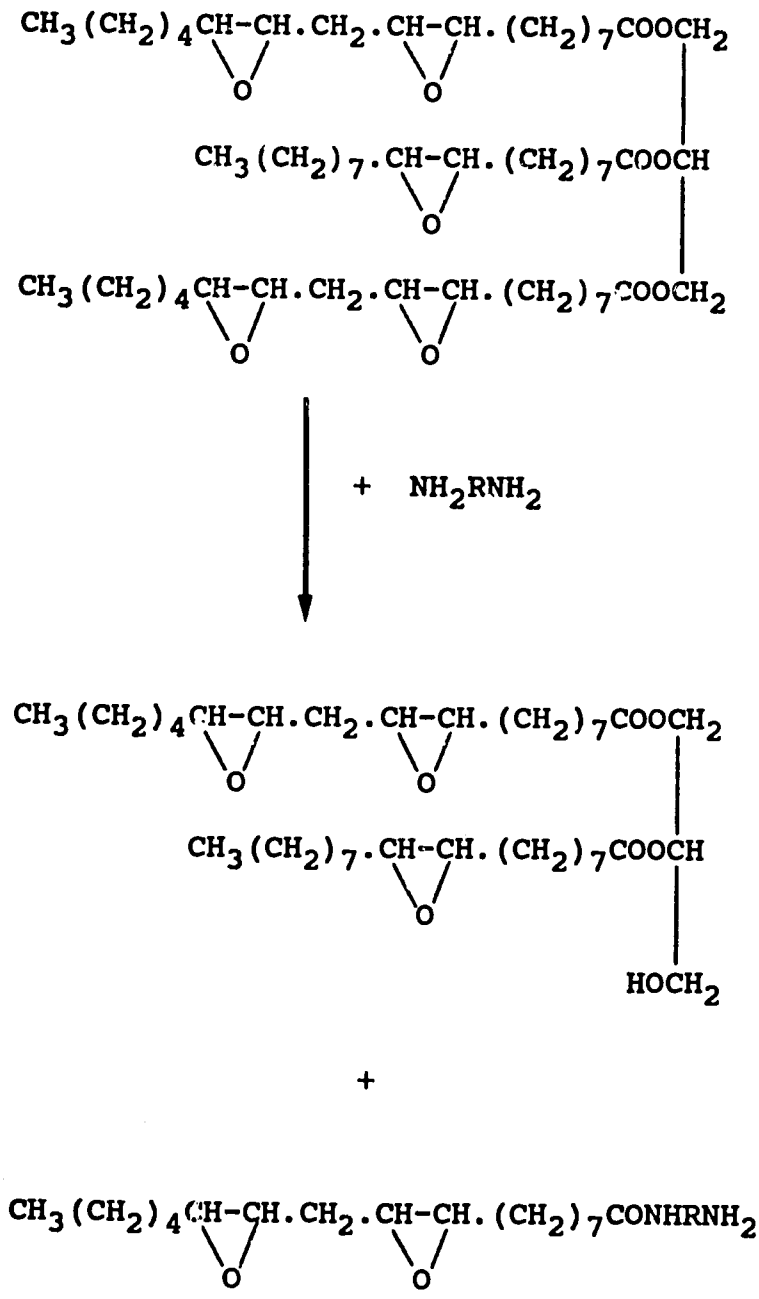


Figure 1. Single-edge-notched (SEN) specimen used for determination of fracture toughness by the three-point bending test. The dimensions are in millimeters.

Figure 2. SEM micrograph of the fracture surface of DGEBA/Isophorone diamine/ESO-20 specimen.

Figure 3. Gel permeation chromatograms of epoxidized soybean oil (A) and liquid rubber (B).

Figure 4. SEM micrograph of the fracture surface of DGEBA/DDM/ESR-15 specimen.

Figure 5. SEM micrograph of the fracture surface of DGEBA/DDM/ESR-20 specimen.

Figure 6. SEM micrograph of the fracture surface of DGEBA/DDM/ESR-30 specimen.

Figure 7. SEM micrograph of the fracture surface of DGEBA/DDS/ESR-10 specimen.

Figure 8. SEM micrograph of the fracture surface of DGEBA/DDS/ESR-20 specimen.

Figure 9. SEM micrograph of the fracture surface of DGEBA/DDS/ESR-30 specimen used for tensile measurements.

Figure 10. SEM micrograph of the fracture surface of DGEBA/DDS/ESR-30 specimen used for fracture toughness measurements.

Figure 11. DMA temperature dependence of the storage dynamic flexure modulus, E' of a pure DGEBA/DDM thermoset (A) and its rubber-modified

DGEBA/DDM/ESR formulations at 15 (B), 20 (C), and 30% (D) rubber content.

Figure 12. DMA temperature dependence of the storage dynamic flexure modulus, E' of a pure DGEBA/DDS thermoset (A) and its rubber-modified DGEBA/DDS/ESR formulations at 10 (B), 20 (C), and 30% (D) rubber content.

Figure 13. DMA tan delta and dynamic mechanical damping peaks of a pure DGEBA/DDM thermoset (A) and its rubber-modified DGEBA/DDM/ESR formulations at 15 (B), 20 (C), and 30% (D) rubber content.

Figure 14. DMA tan delta and dynamic mechanical damping peaks of a pure DGEBA/DDS thermoset (A) and its rubber-modified DGEBA/DDS/ESR formulations at 10 (B), 20 (C), and 30% (D) rubber content.

Figure 15. DSC curve of epoxidized soybean liquid rubber.

Figure 16. Dependence of Young's modulus on the ESR rubber content of the DGEBA/DDM/ESR (A) and DGEBA/DDS/ESR formulations (B).

Figure 17. Infrared spectra of pure epoxidized soybean oil (A) and its liquid rubbers with DDM after prepolymerization at 135°C for 0 (B), 24 (C), and 48 hours (D).

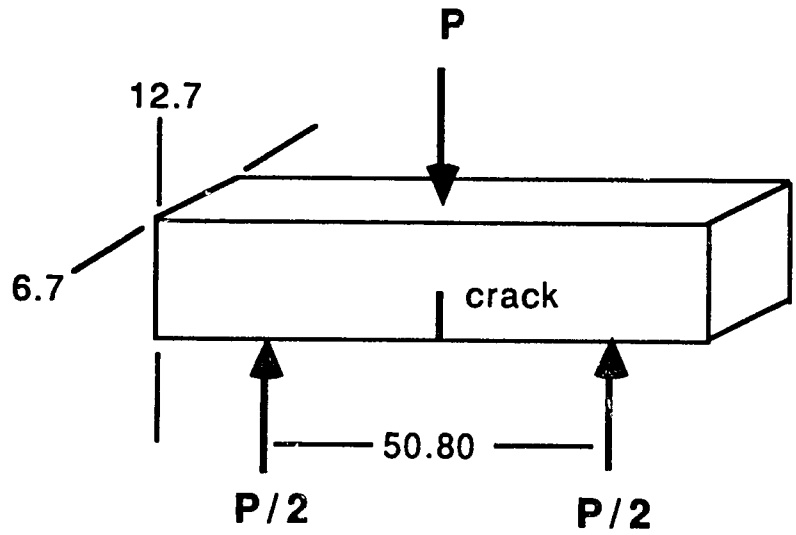


FIGURE 1

FIGURE 2

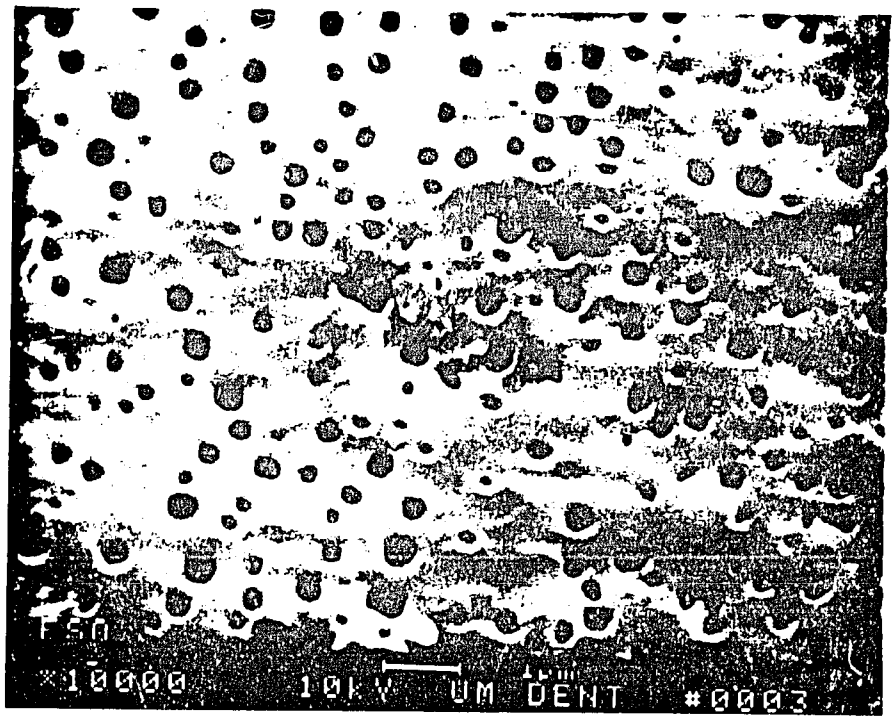
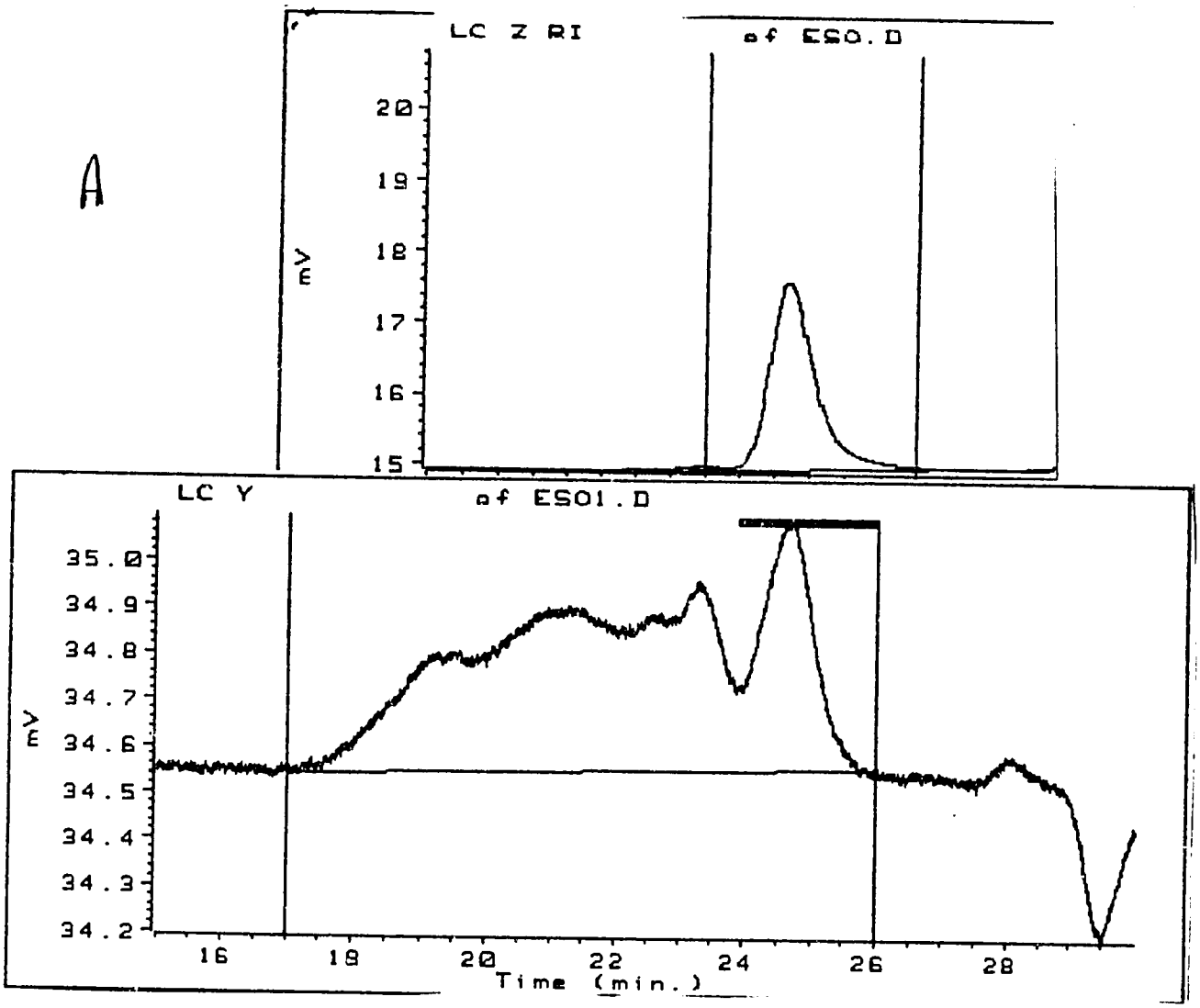


Figure 3

A

B


LC Z RI
of ES0.D
20
19
18
17
16
15
mV
LC Y
of ES01.D
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34.7
34.6
34.5
34.4
34.3
34.2
mV
16
18
20
22
24
26
28
Time (min.)

FIGURE 4

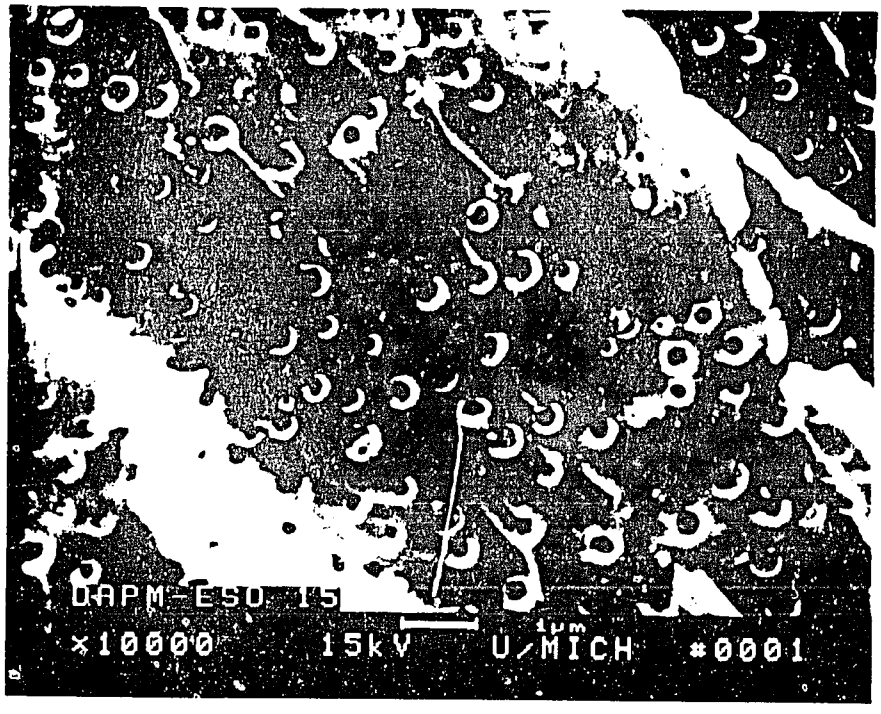

FIGURE 5

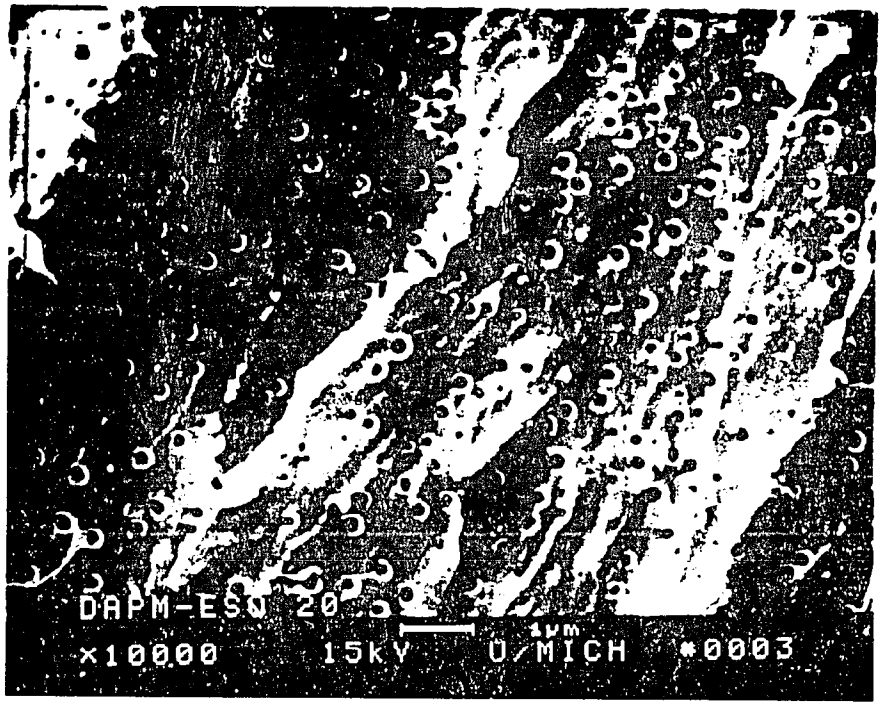

Figure 6

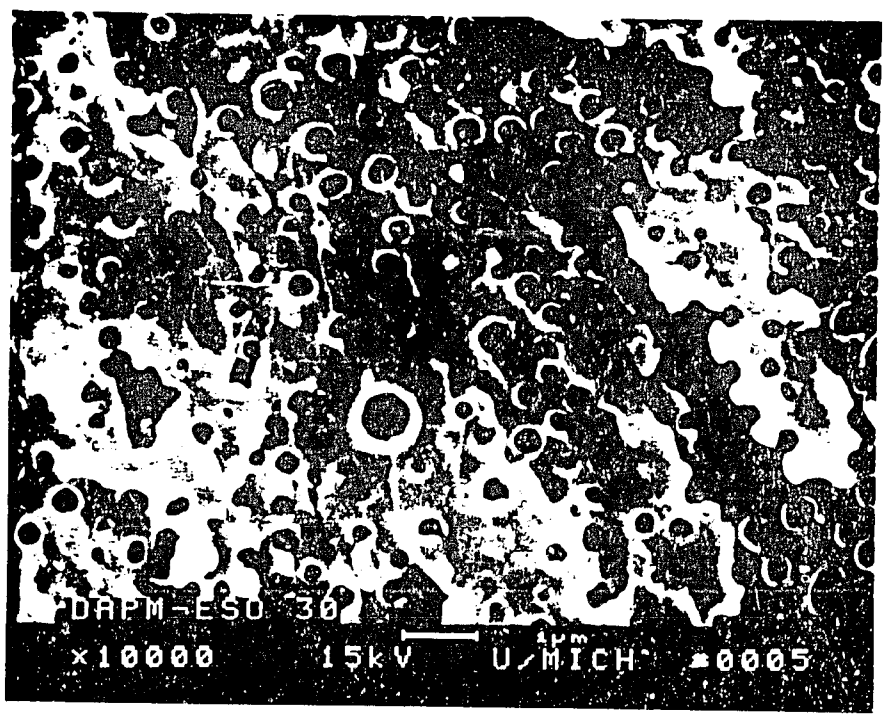

Figure 7

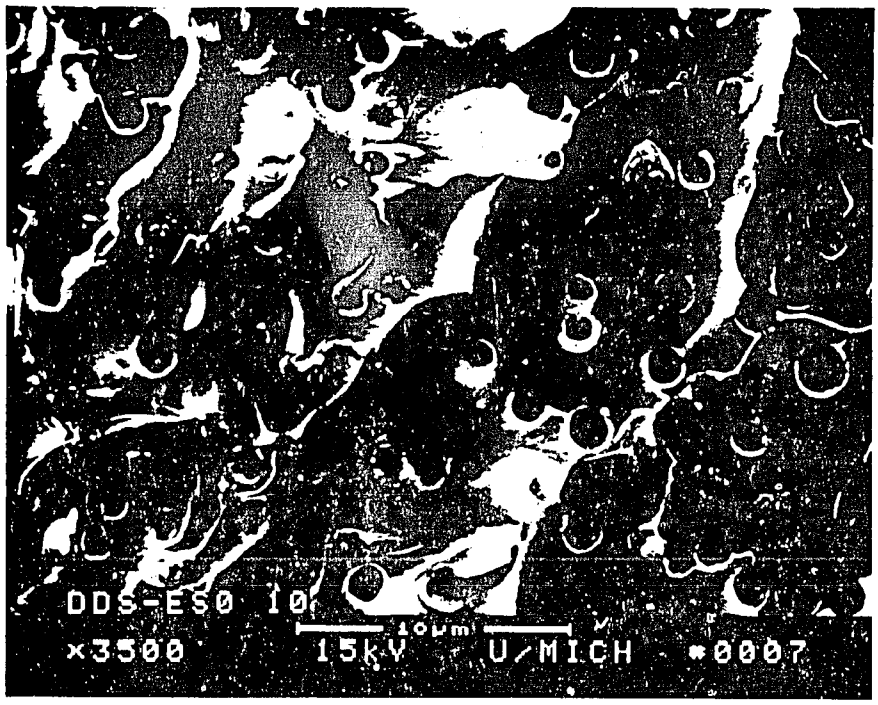

FIGURE 6

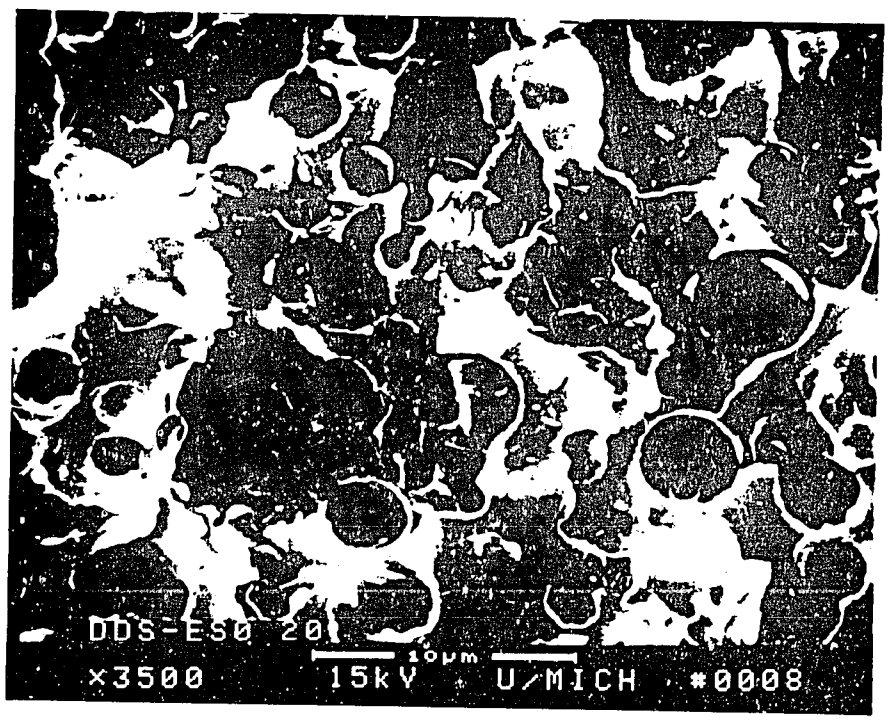

FIGURE 9

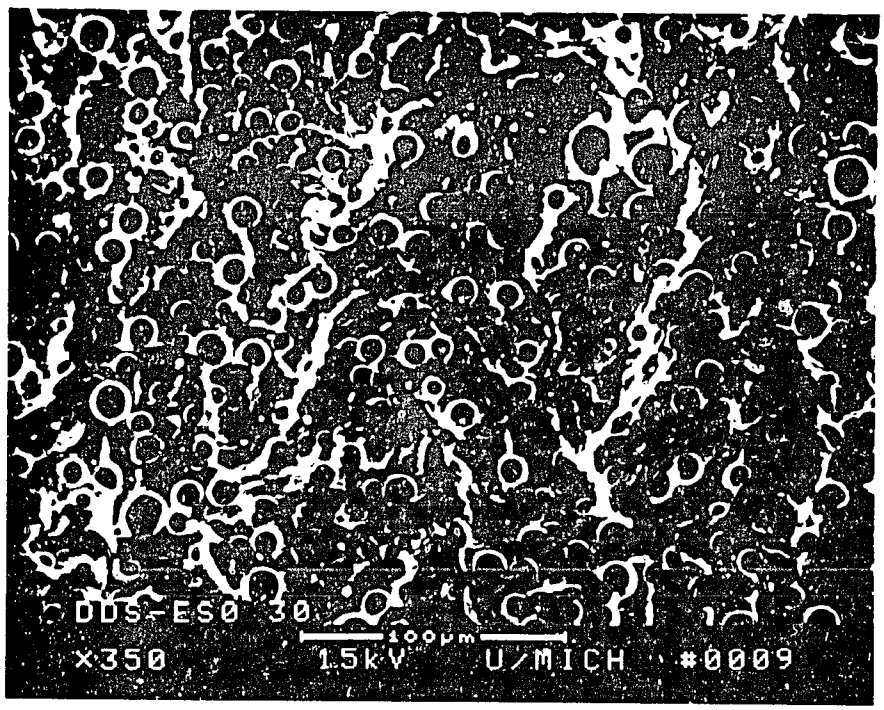

Figure 1.)

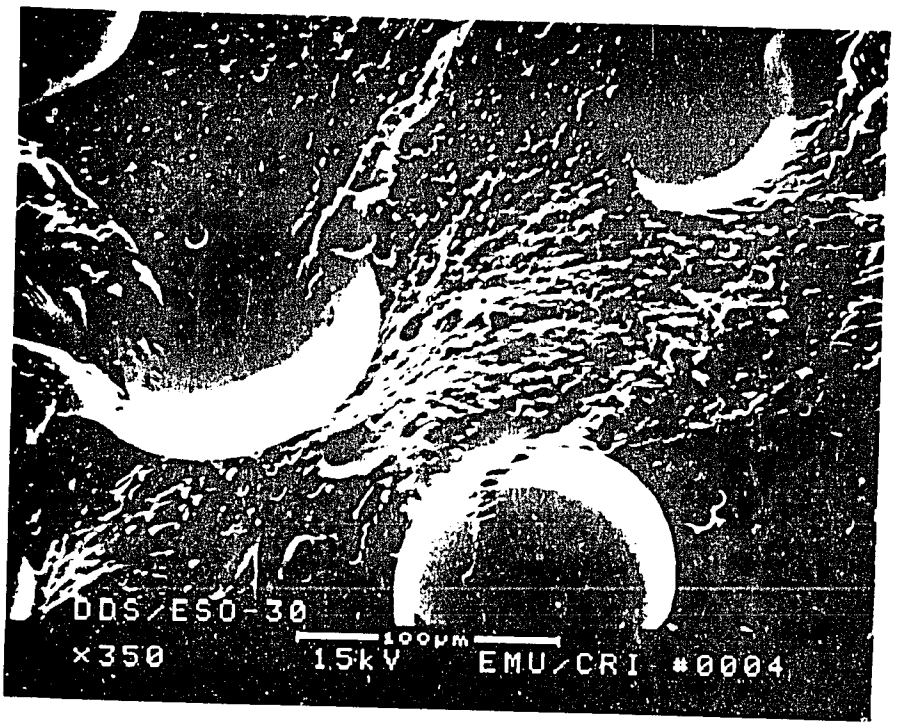

FIGURE 11

Sample : EPOXY/DAPM/ESBE[illegible]%H70+2H150
Size : 32.[illegible] x 7.[illegible] x 3.[illegible]800 mm
Method : FROM-130TO200 2DEG/MIN
Comment: TORQUE 10 IN-LB LENGTH CORRECTION

DMA

File : C: IFESO.1[illegible]
Operator: I.FRISCHINGER
Run Date: [illegible]Apr9901[illegible]

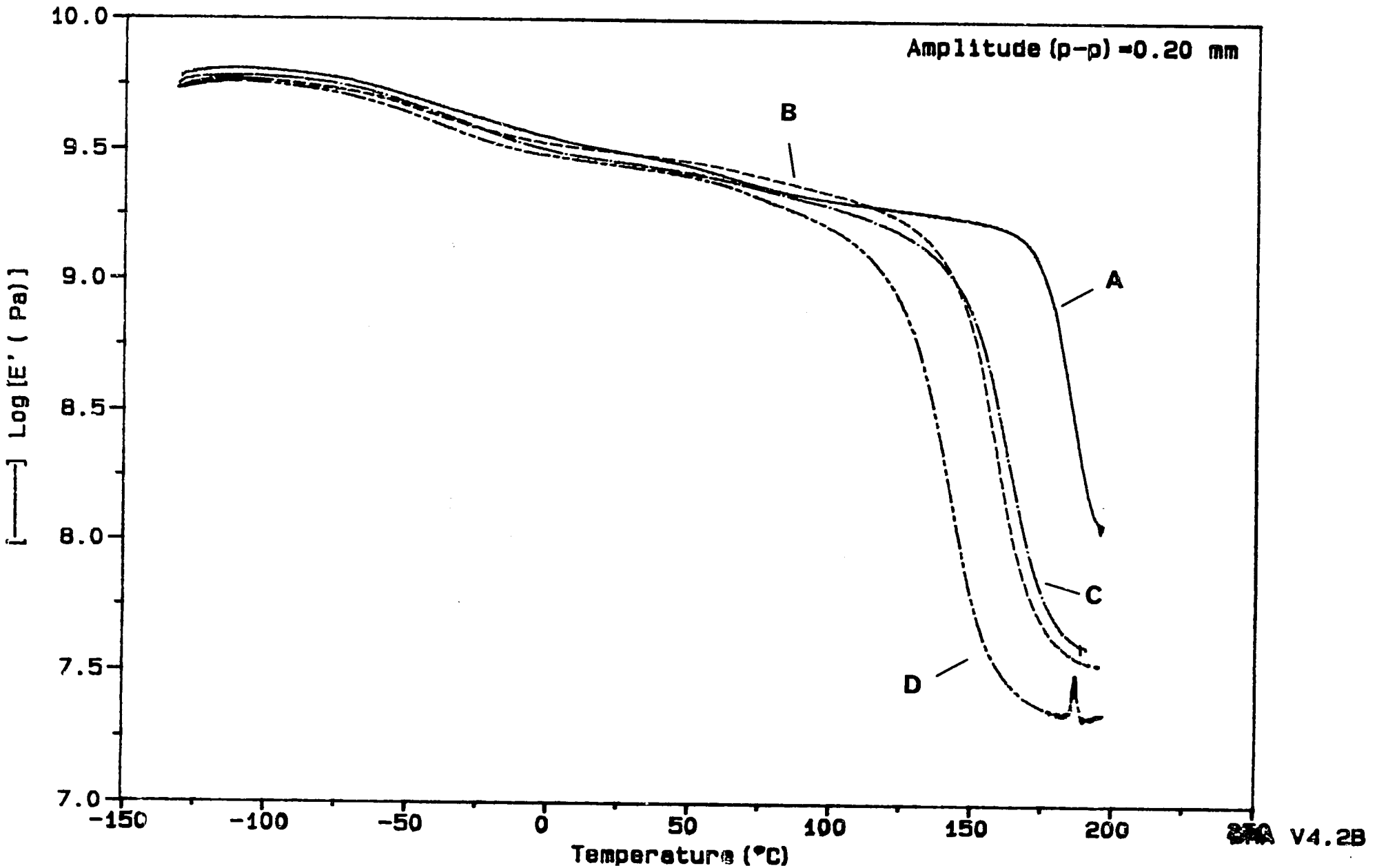

Figure 12

Sample : EPOXY/DDS/E88E8028H150
Size : 28.58 x 7.68 x 2.8800 mm
Method : FROM-130TO280 2DEG/MIN
Comment: COBQUSG1QTIN4BB GBNGUH18ORBEGTION

DMA

File : C:DB6S0.08
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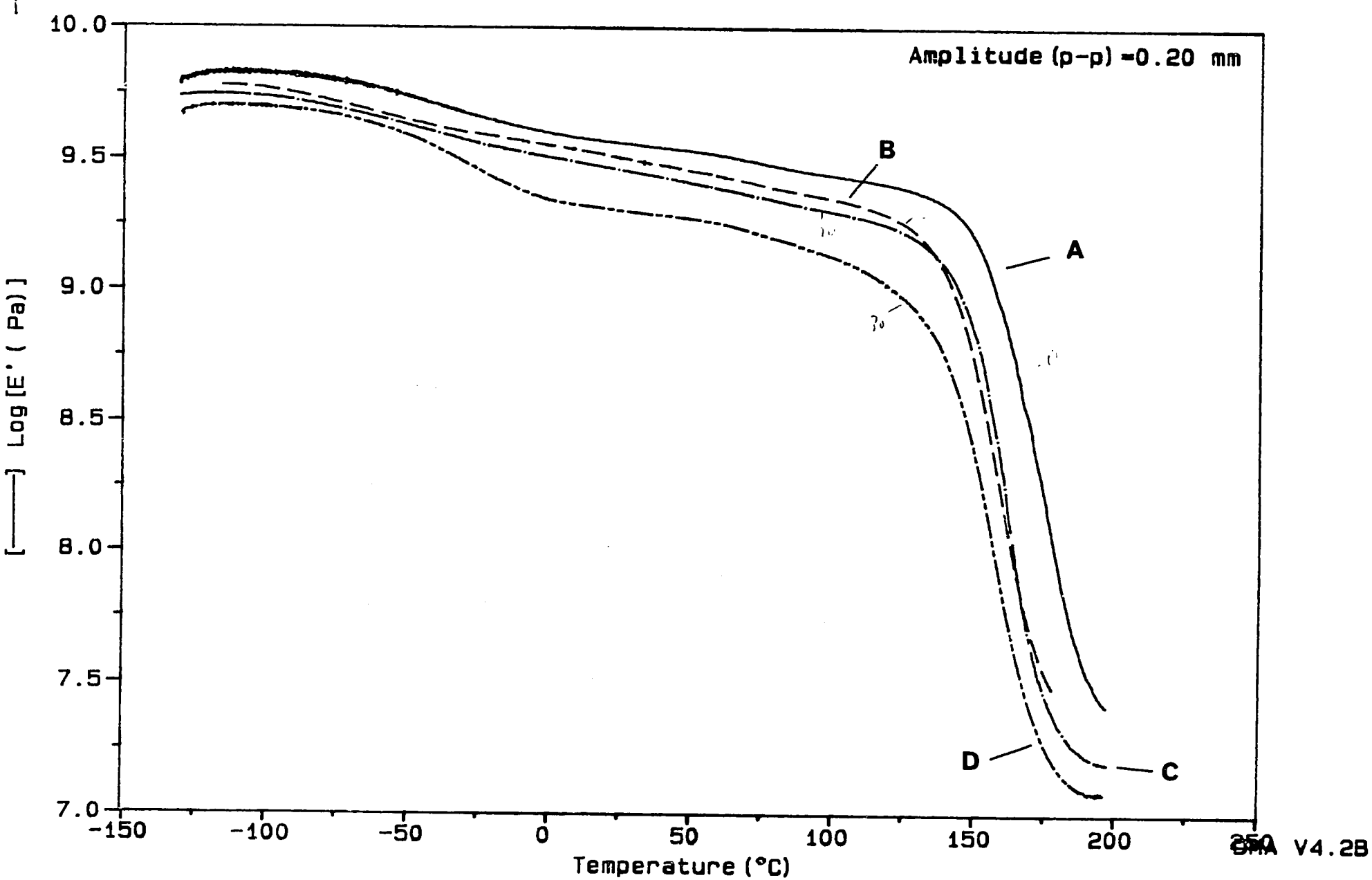

Figure 13

Sample : EPOXY/DAPM/E88E80%H70+2H150
Size : 32.88 x 7.80 x 3.2800 mm
Method : FROM-130TO200 2DEG/MIN
Comment: TORQUE 10 IN-LB LENGTH CORRECTION

DMA

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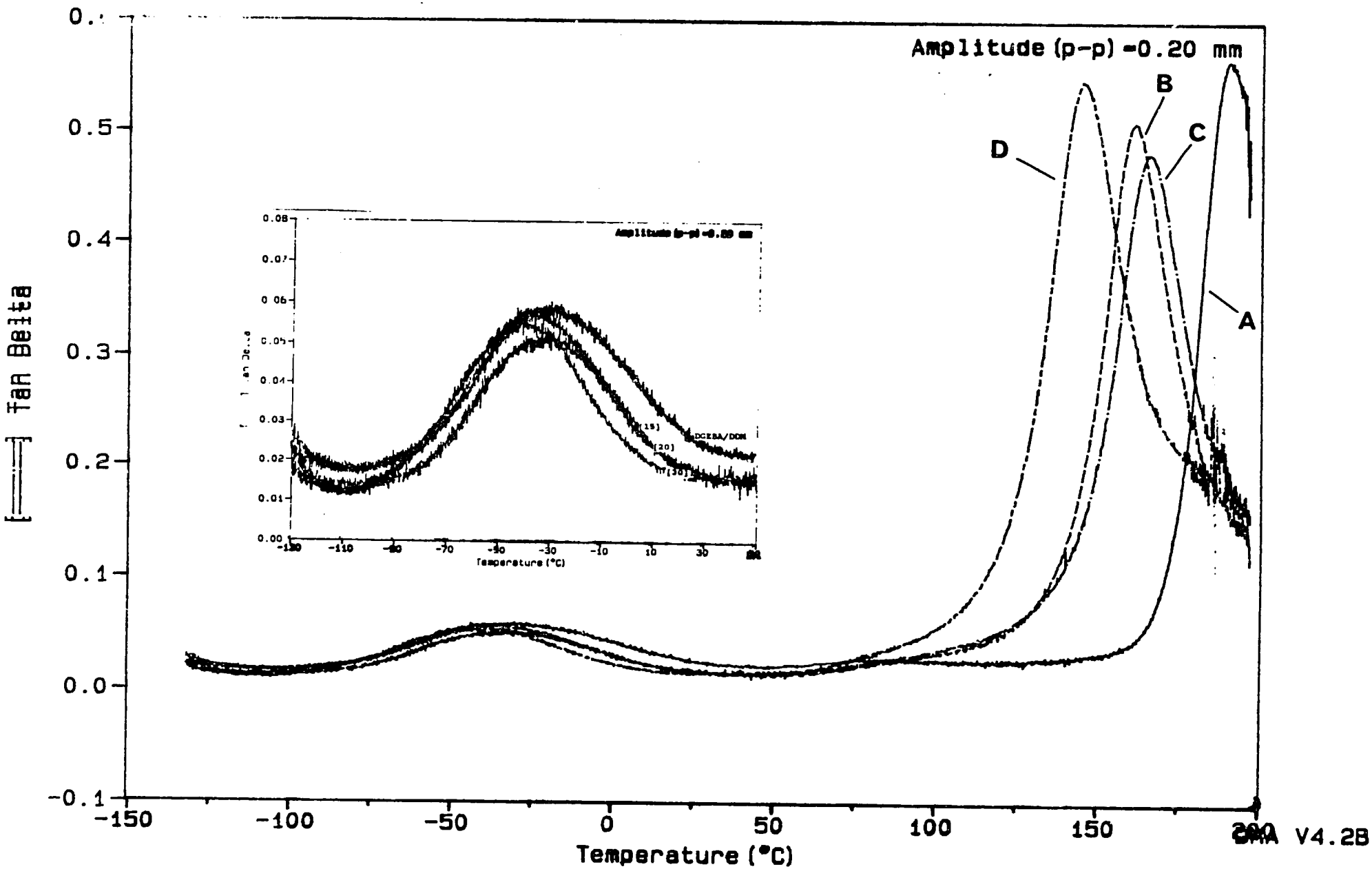


PART OF FIGURE 13

Sample : EPOXY/DAPM/ESO 15%
Size : 31.53 x 7.16 x 3.5600 mm
Method : FROM-130TO200 2DEG/MIN
Comment: TORQUE 10 IN-LB LENGTH CORRECTION

DMA

File : C:IFESO.10
Operator: I.FRISCHINGER
Run Date: 27-Apr-90 12:18

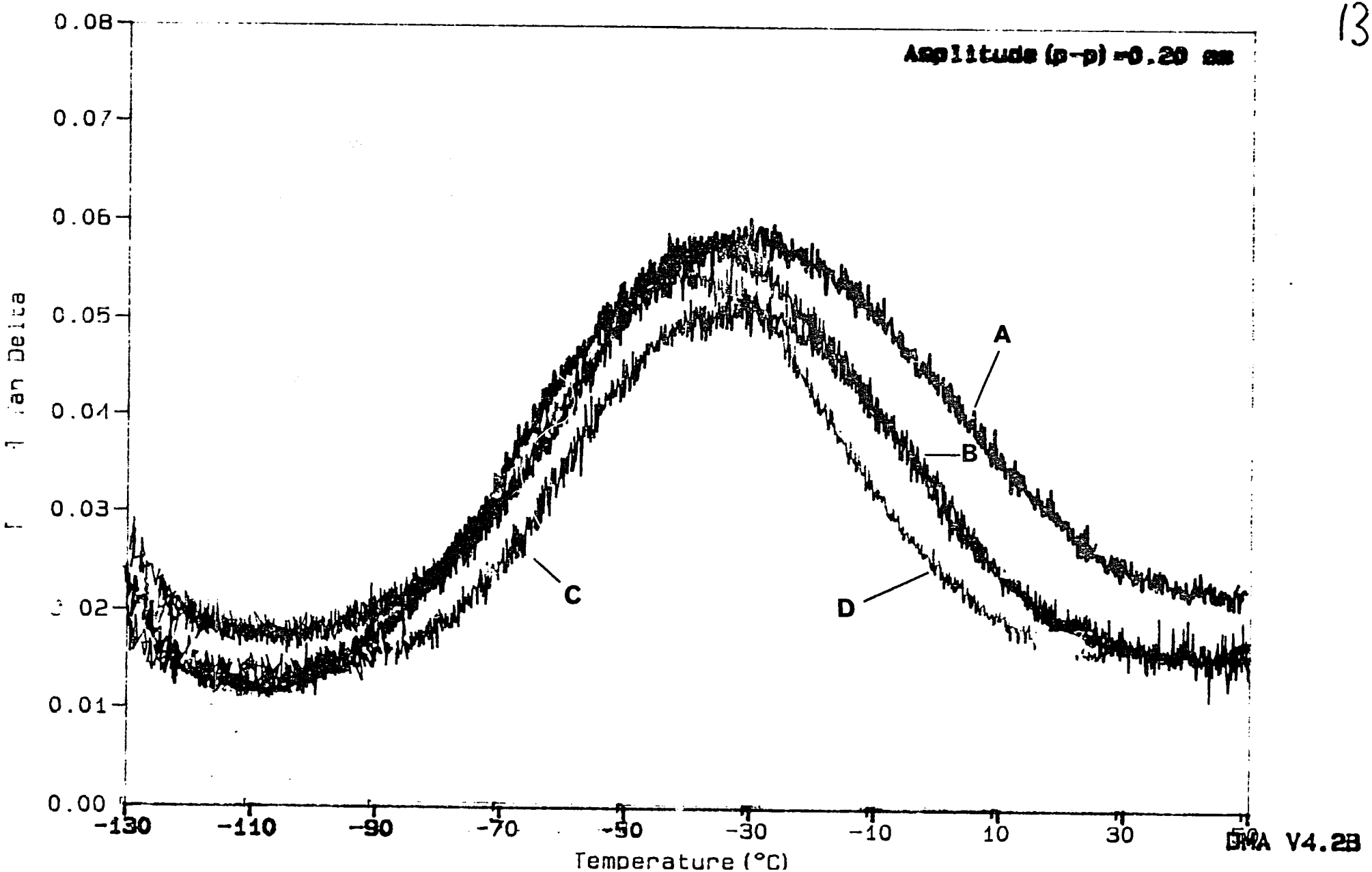
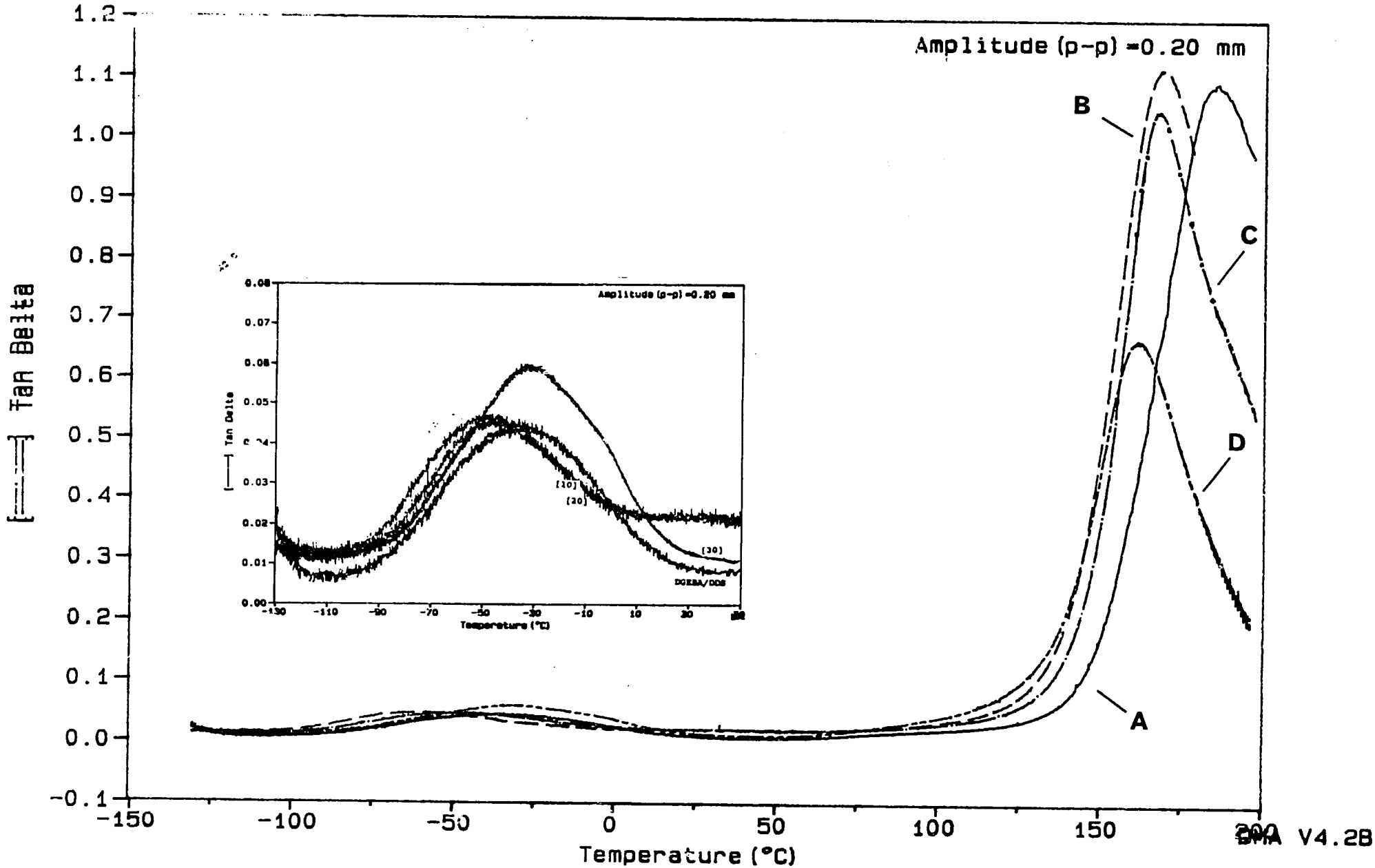


FIGURE 14

Sample : EPOXY/DDS/E88E80%H150
Size : 28.00 x 7.00 x 2.0000 mm
Method : FROM-130TO280 2DEG/MIN
Comment: COBQUBG10TIN4BB GBNGOH180RBEGTION

DMA

File : C:DB650.00
Operator: I.FRISCHINGER
Run Date: 06Apr9801:52:00



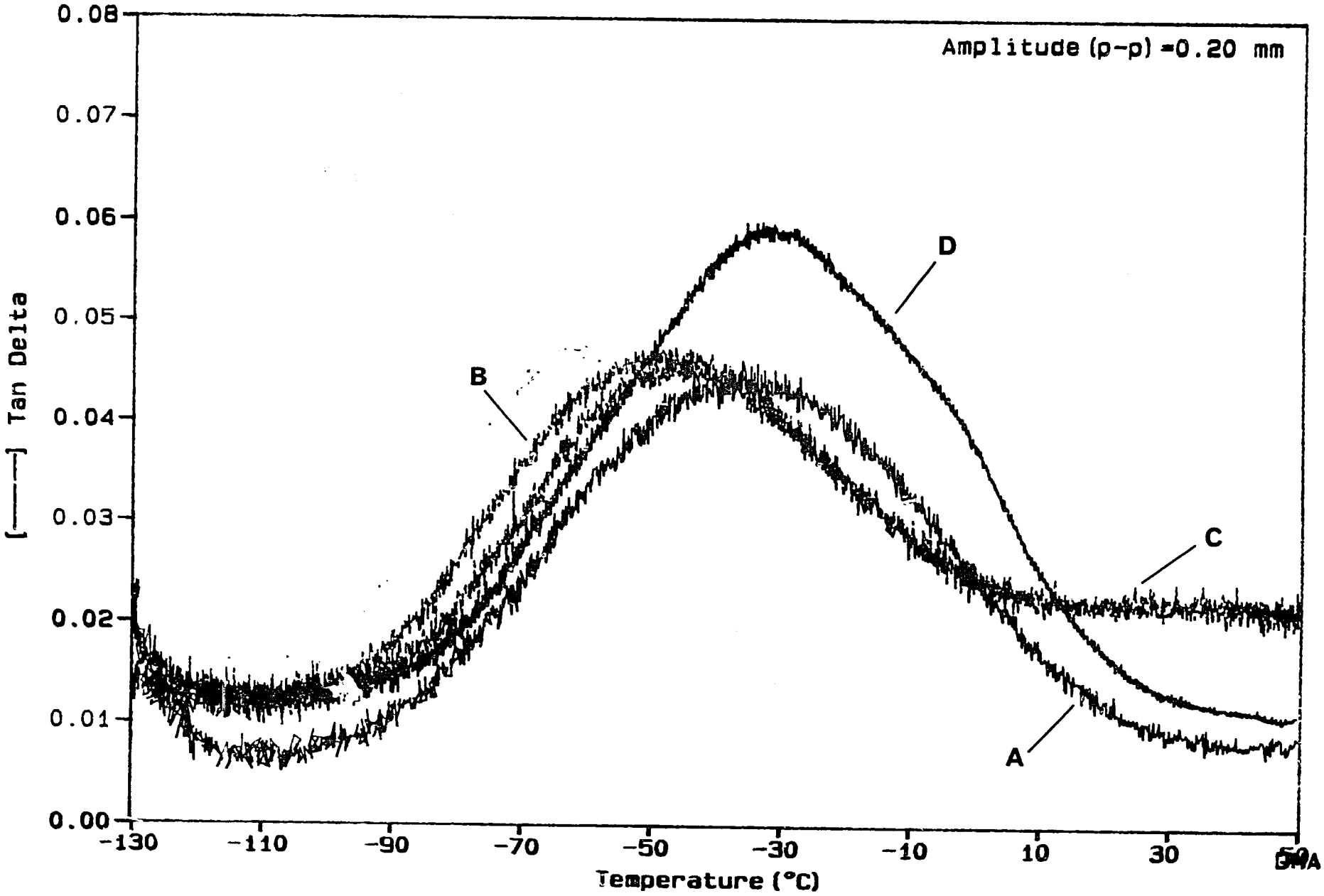
DMA V4.2B

part of Figure 14

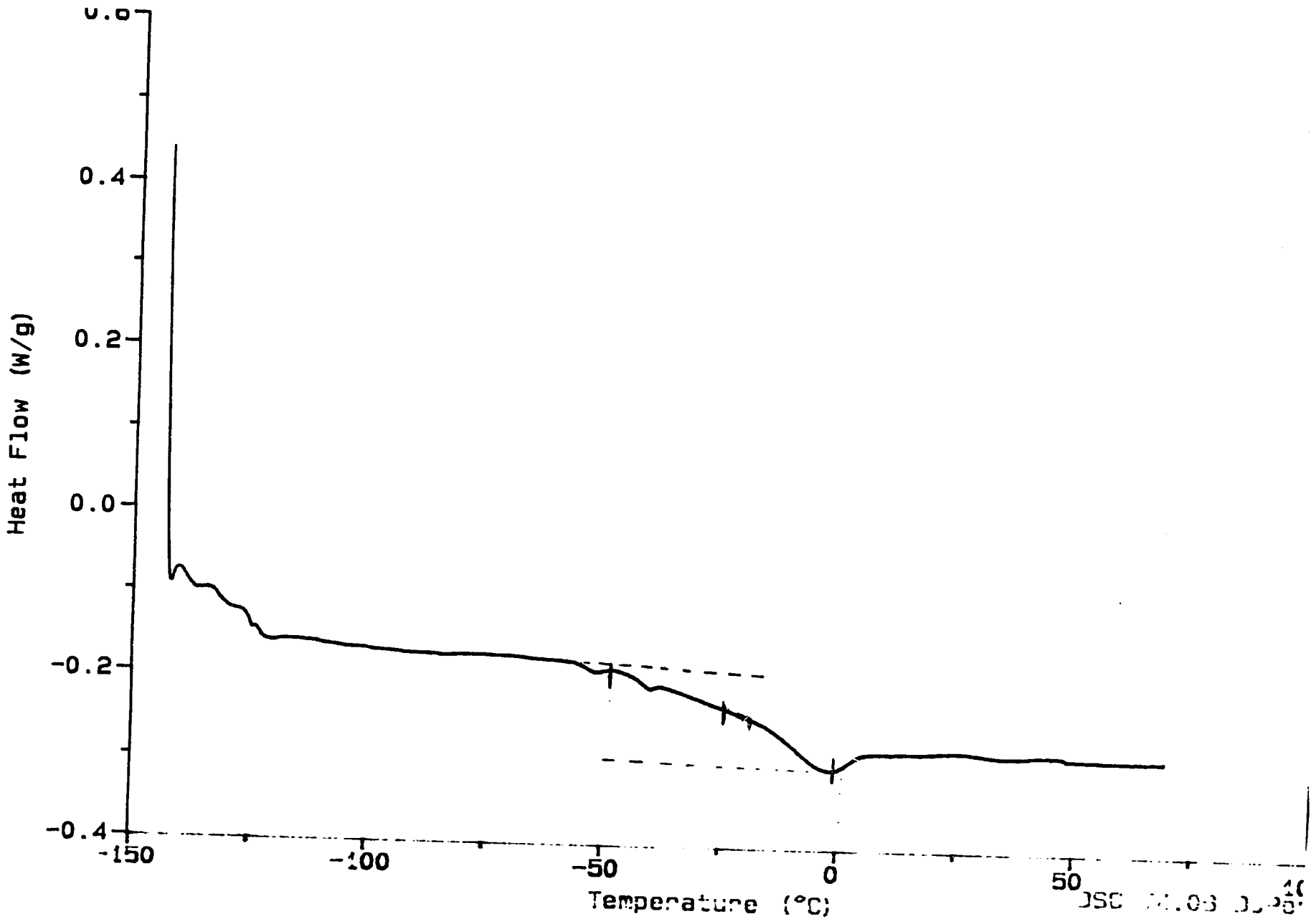
Sample : EPOXY/DDS/E88E202H150
Size : 32.06 x 7.00 x 2.0800 mm
Method : FROM-130TO200 2DEG/MIN
Comment: TORQUE 10 IN-LB LENGTH CORRECTION

DMA

File : C:IFESO.00
Operator: I.FRISCHINGER
Run Date: 06Aug90 17:28:06



DMA V4.2B


0.6
0.4
0.2
0.0
-0.2
-0.4
Heat Flow (W/g)
-150
-100
-50
0
50
Temperature (°C)

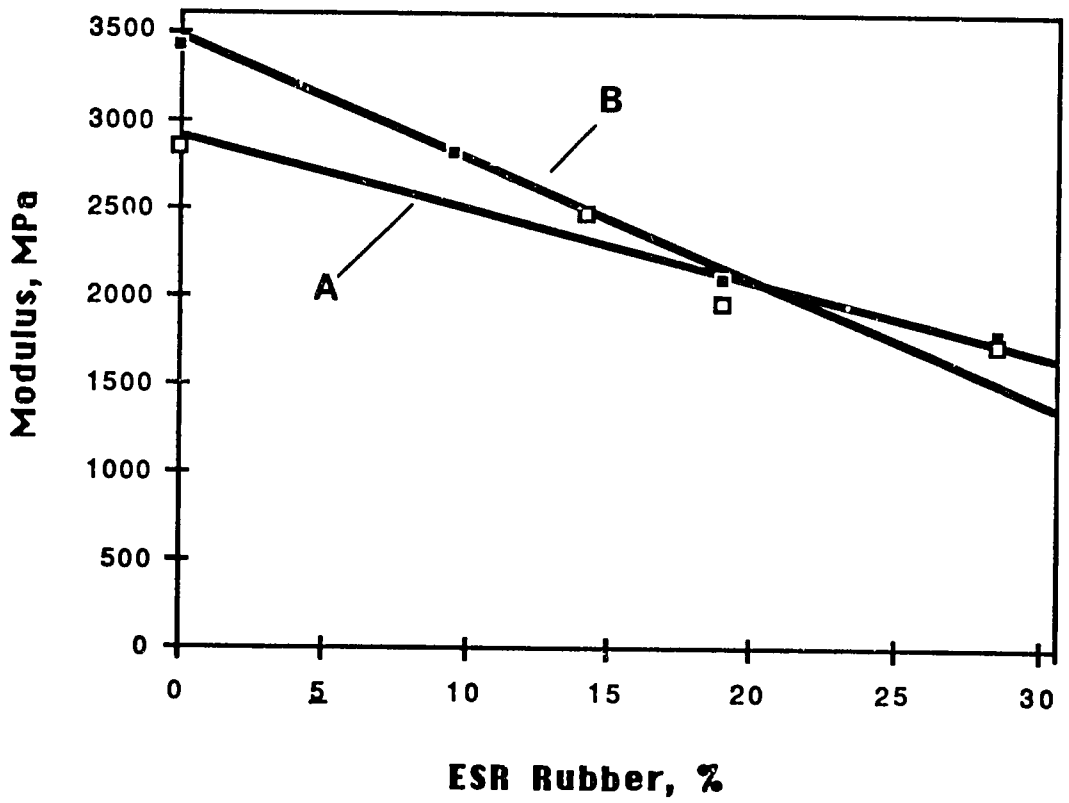

3500
3000
2500
2000
1500
1000
500
0
Modulus, MPa
B
A
0
5
10
15
20
25
30
ESR Rubber, %

FIGURE 16.

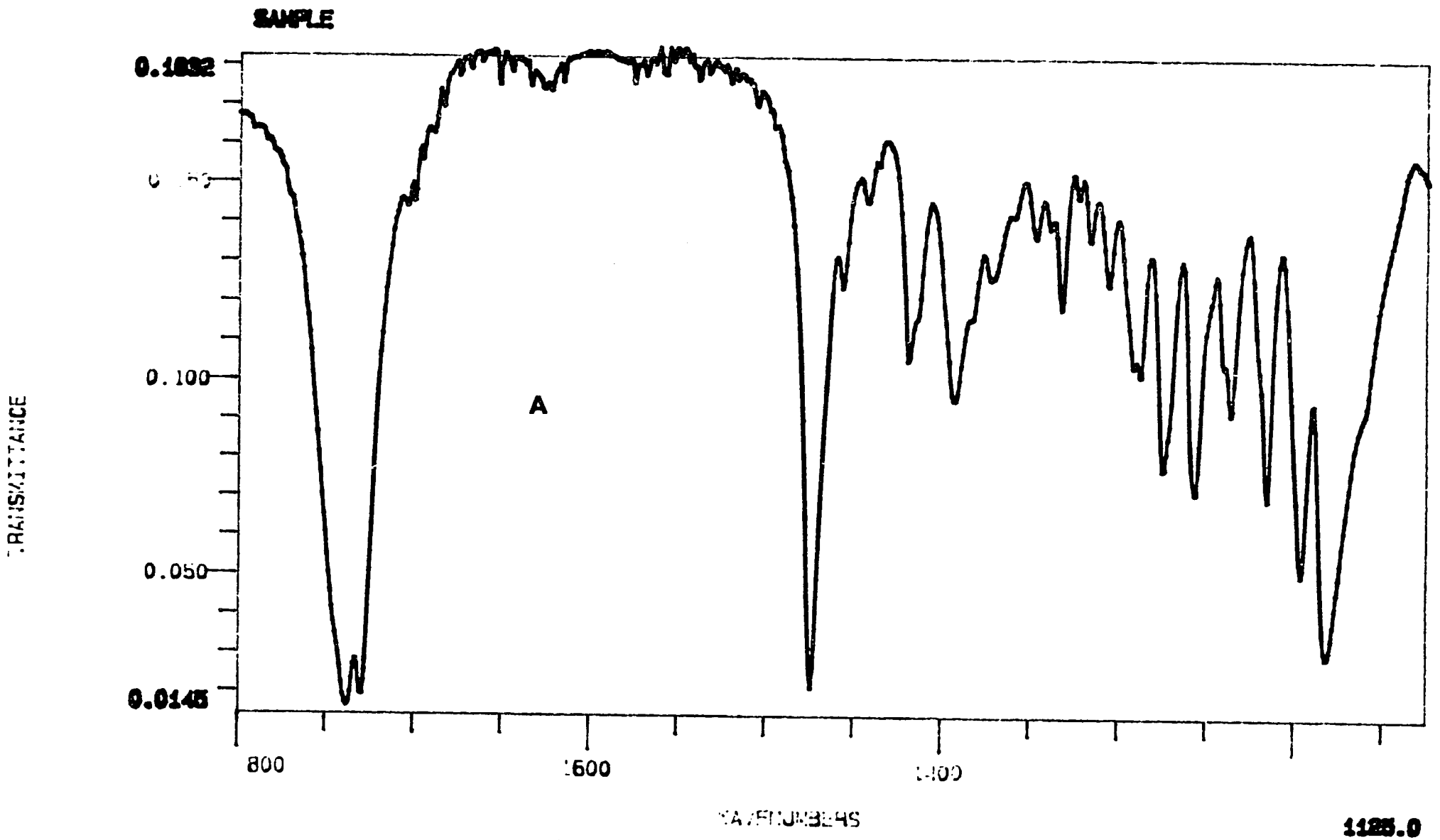


Figure 17.

IBM Instruments Inc.

(A)

Pat atn.

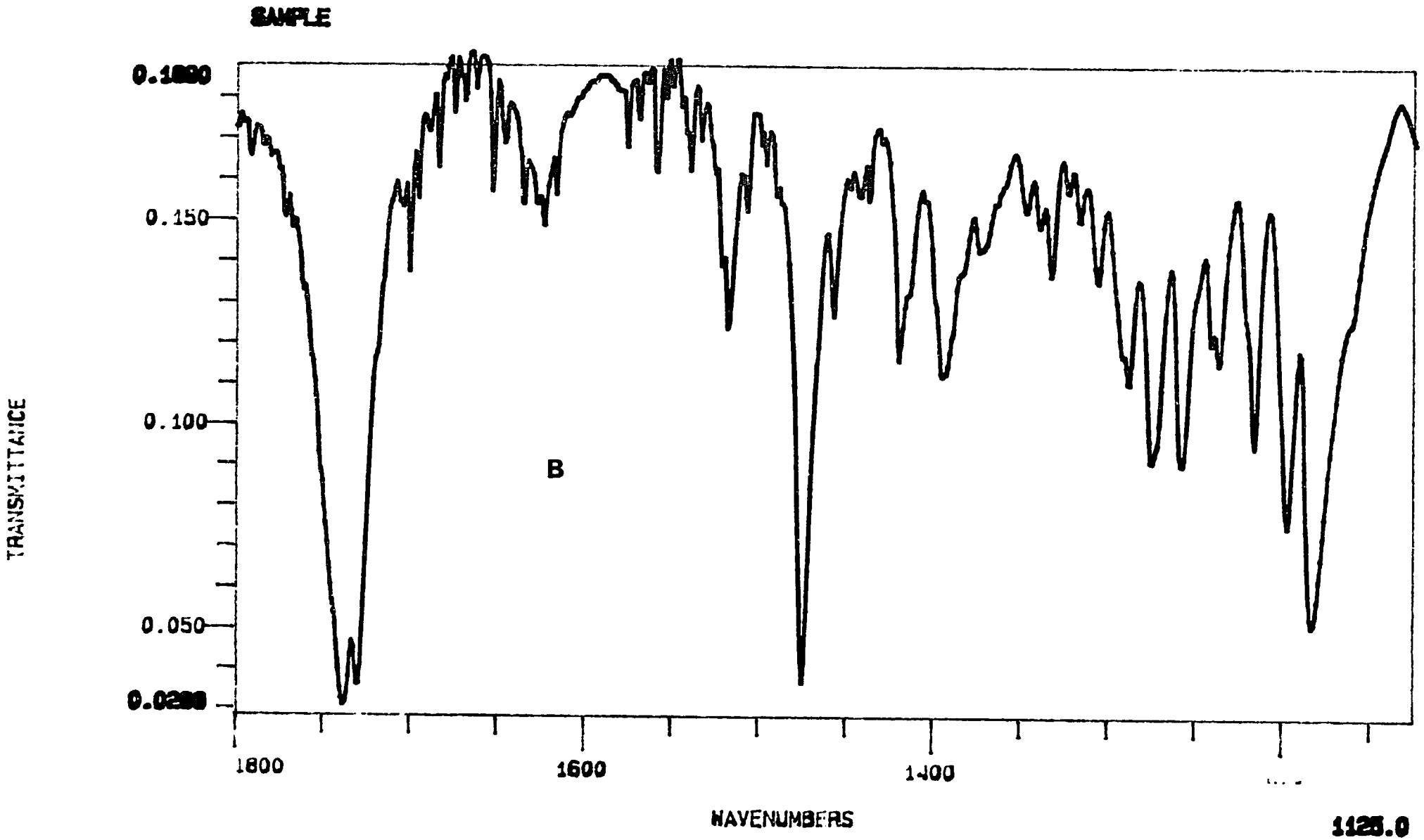
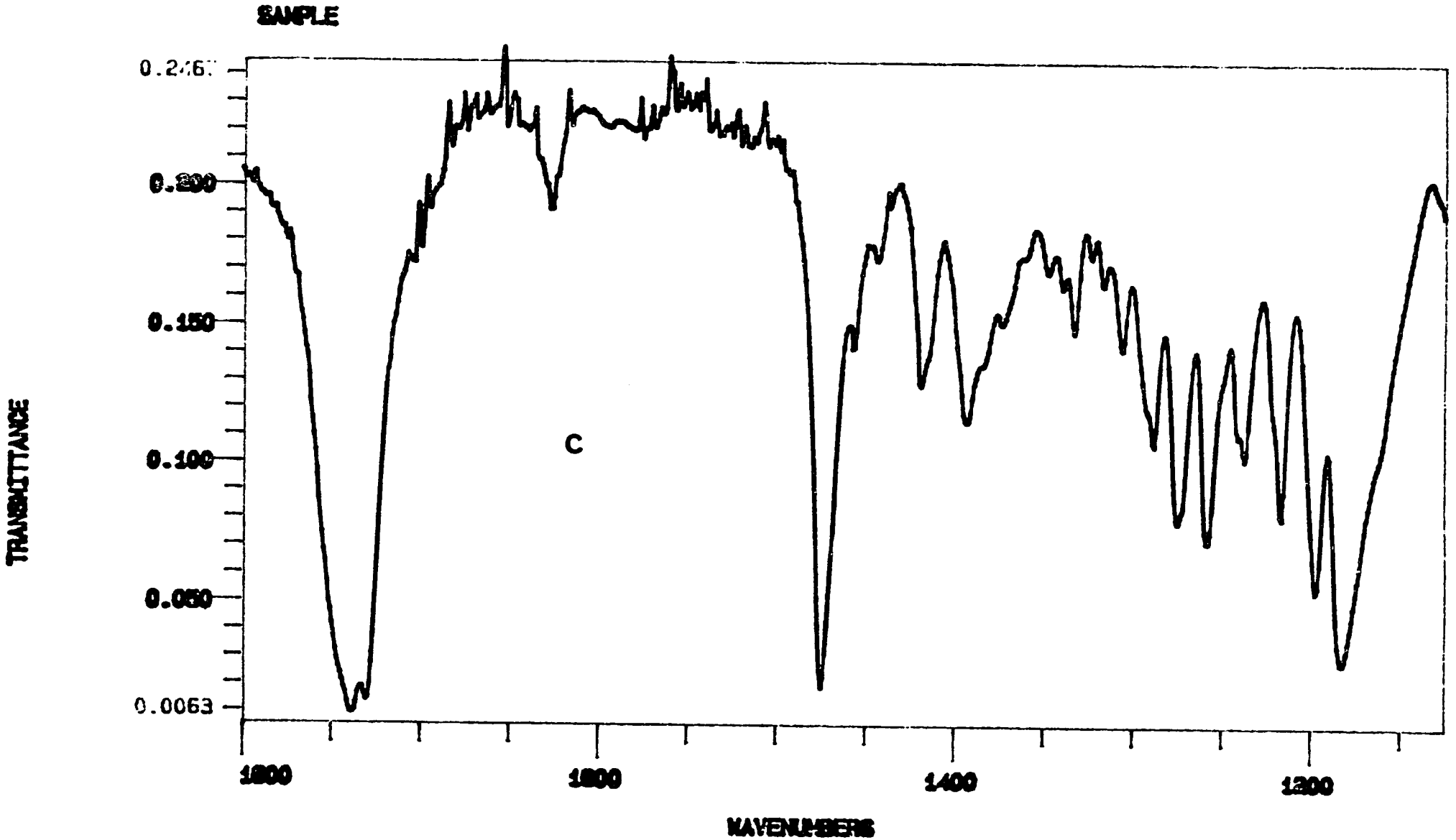


FIGURE 17

IBM Instruments Inc.

B

mixture
Chrom

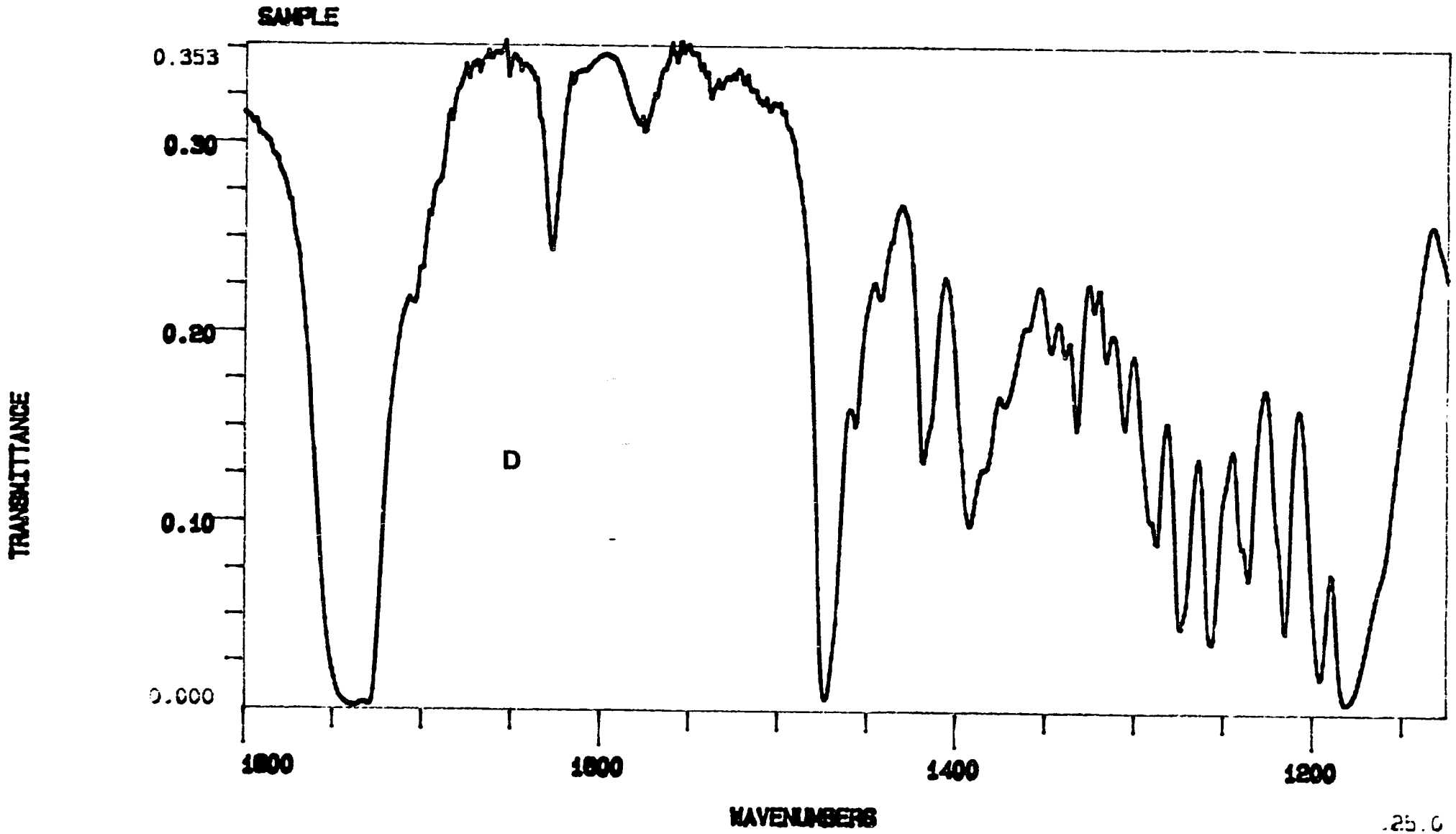


mixture
24 hours

IBM Instruments Inc.

Figure 17

(c)



mixture
48 hours

FIGURE 17

D

IBM Instruments Inc.

13. S. Dikikov, M.S. Islam, Il Frischinger, T. Lepkowski, and P. Muturi, Vernonia Oil: A New Reactive Diluent for High Solids Alkyd and Epoxy Resins and Coatings, 18th Annual Waterborne, Higher-Solids, and Powder Coatings Symposium, New Orleans, LA, February 1991.

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PROCEEDINGS OF THE EIGHTEENTH
WATER-BORNE, HIGHER-SOLIDS, AND POWDER COATINGS SYMPOSIUM

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A Symposium Co-Sponsored by

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VERNONIA OIL: A NEW REACTIVE DILUENT FOR HIGH SOLIDS ALKYD AND EPOXY RESINS AND COATINGS

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Presented at the
Water-Borne, Higher-Solids, and Powder Coatings Symposium
February 6-8, 1991

Symposium Sponsored by
The University of Southern Mississippi
Department of Polymer Science
and
Southern Society for Coatings Technology

ABSTRACT

Vernonia oil has been evaluated for preparation of high solids coatings formulations by replacing conventional solvents. Vernonia oil is a natural epoxidized vegetable oil at a developmental stage in several countries. Trivernolin, the principal triglyceride, has a unique structure with three reactive epoxy groups and three carbon-carbon double bonds per molecule. Vernonia oil is characterized by very low viscosity, lower m.p., homogeneous molecular structure and potentially low price. It appears to be an attractive reactive diluent for low VOC alkyd and epoxy resins and coatings applications.

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INTRODUCTION

There is an urgent need for reactive diluents for the reduction of conventional non-reactive solvents in coating formulations for air pollution control. Recently, further and stricter measures have been taken for reduction of air pollution. In 1988, the U.S. Environmental Protection Agency announced a ban on construction of major air-polluting plants in Los Angeles and other U.S. cities, and in the same year the South Coast Air Quality Management District announced a plan for reduction of hydrocarbon emissions in Orange County, California by 80 to 90% over the next five years. This plan requires reduction of volatile organic compound (VOC) emissions from paints and varnishes from the current 22.1 tons per day to 2.9 tons per day several years from now. It is an impossible task with today's coatings technology.

The objective of our research is the application of vernonia oil as a reactive diluent for high solids alkyd, epoxy, and epoxy-ester coating formulations by replacing conventional solvents which produce VOC emissions.

Vernonia oil, which is a naturally occurring epoxidized vegetable oil, contains predominantly trivernolin, a triglyceride of vernolic acid (Figure 1). Trivernolin contains three epoxy rings and three carbon-carbon double bonds per triglyceride molecule. There is one epoxy ring and one carbon-carbon double bond per each vernolic acid residue. Vernolic acid constitutes about 80% of the fatty acid residues of vernonia oil triglycerides.

VERNONIA GALAMENSIS

Vernonia galamensis, the source of vernonia oil, is a new potential oil seed crop for frost-free areas (Ref. 1-6). Some varieties grow in arid and semi-arid areas of the tropics and sub-tropics on land that is unsuitable for food crops. It is an annual weed. It has good seed retention and seeds germinate easily. It also has natural resistance to disease, nematodes, and most insects. Neither wild nor domestic animals consume Vernonia galamensis.

"Vernonia" seeds contain about 42% oil in contrast to soybeans, which contain only 17% oil. The maximum seed yield reached at this development stage is 2227 pounds per acre which compares favorably with an average yield of 1,926 pounds per acre for soybeans in the U.S. in 1979, the best yield for this crop in the U.S. from 1971 through 1984 (Ref. 2). Increased yields of vernonia seed are expected by breeding as greater genetic diversity becomes available.

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In summary, it appears that the major agronomic problems for cultivation have been resolved. This new crop is currently at a developmental stage in several African countries, especially in Zimbabwe and Kenya and it has the potential to become a major industrial crop. Several major chemical and coatings companies have expressed strong interest in vernonia oil. Rhône-Poulenc (U.S.A. division) has started experimental crop trials for vernonia oil production, and several tons of Vernonia galamensis seeds are being harvested this year. Cargill is evaluating the possibilities for cultivation of Vernonia galamensis and the potential use of vernonia oil as well.

RESULTS AND DISCUSSION

Properties of Vernonia Oil. Vernonia oil has several unique features:

a. It is a transparent homogeneous liquid at room temperatue with excellent solubility in many organic solvents, diluents, and paints.
b. Vernonia oil has a low viscosity of 300 cps at 50°F and 100 cps at 85°F.
c. It has a low melting point of -36°F.
d. Vernonia oil has a homogeneous molecular structure consisting predominantly of identical triglyceride molecules which have three equal vernolic acid residues. In contrast, all other vegetable oils consist of a heterogeneous mixture of triglycerides with different fatty acid residues.
e. It is expected to be available at a low price in the range of $1.00-1.50 per pound.
f. Toxicity of vernonia oil is expected to correspond to that of the epoxidized soybean and linseed oils which are industrially produced.

Vernonia vs. Other Epoxidized Vegetable Oils. We believe that vernonia oil does not compete with other epoxidized vegetable oils, i.e. epoxidized soybean oil and epoxidized linseed oil, which are industrially produced by epoxidation of unsaturated vegetable oils and have structures similar to vernonia oil. Epoxidized soybean and linseed oils are less suitable for coatings applications as reactive diluents because of their higher viscosity.

Both epoxidized soybean oil and linseed oils have higher viscosity, i.e. in the range of 1000 - 2000 cps at 50°F, in contrast to 300 cps for vernonia oil. Both are heterogeneous semi-solids even at 75°F and form homogeneous, clear liquids only above 85°F. Their applications require a warming procedure at 120°F with mild agitation prior to use for at least one hour.

The difference in viscosity of vernonia oil and epoxidized soybean oil is rather surprising since both have similar molecular structures. Initially, we thought that soybean oil partially polymerizes during the epoxidation reaction and the resulting epoxidized soybean oil contains a certain amount of oligomers which increases its viscosity. GPC of vernonia oil and epoxidized soybean oil, however are identical (Figure 2). Evidently, both oils have exactly the same molecular weight distribution and the low viscosity is an inherent characteristic of vernonia oil.

Drying Mechanism of Vernonia Oil. Carlson and co-workers (Ref. 7) have reported that "vernonia" coatings can be obtained directly from vernonia oil by a standard baking procedure at 150° for 30 minutes in the presence of different drier systems.

We were interested in the drying mechanism of vernonia oil since it has two functionalities: unsaturated double bond and epoxy ring. For this purpose, we have compared the drying characteristics of triolein, vernonia oil, and epoxidized soybean oil in the presence of 0.5 per cent cobalt drier under baking conditions at 150°C for one hour. The molecular structure of these three oils is shown in Figure 1.

Epoxidized soybean oil does not form coatings at 185°C for several hours. Obviously, its epoxy groups do not polymerize under these conditions.

Both triolein and vernonia oil form good coatings. These results show that vernonia oil drying is based on its unsaturated carbon-carbon double bonds and not on its epoxy functionality. This allows its application as a reactive diluent, not only in epoxy and epoxy-ester formulations, but in alkyd resins as well.

Results also show that vernonia oil dries at lower temperature and much faster than triolein. Good coatings have been obtained from vernonia oil at 150°C for half an hour. Triolein does not form coatings at 150°C for 1 hour. It forms coatings only at 180°C for 1.5 hours. The epoxy rings of vernonia oil probably activate the oxidation of the methylene group between the epoxy ring and the carbon-carbon double bond and therefore dries faster than triolein.

Compatibility with Alkyd Resins. We carried out compatibility studies with Reichhold Beckosol long oil alkyds 10-560 and 10-060, medium oil alkyd 11-035, and short oil alkyd 12-005. Vernonia oil is compatible with all three types of alkyd resins at any ratio.

Drier Evaluation. We evaluated different driers and drier combinations for vernonia oil and for its 20% mixtures in alkyd resins (Table 2). Cobalt drier at 0.1 per cent concentration forms good coatings at 150°C for 1 hr. Zirconium drier does not form coatings even at higher concentration (0.5%), higher temperature (160°C) and longer time (2 hours). Calcium and manganese driers have intermediate activity, weaker than the cobalt drier but stronger than the zirconium. Without going into further detail, Manchem Manosec CD-44 drier gives the best results. It is more active than all other driers and drier combinations. It contains cobalt (0.6%), calcium (0.2%), and lithium (0.03%) carboxylates in mineral spirits.

Vernonia oil does not air dry with none of the driers at room temperature for several hours. In the presence of Manosec CD-44 it dries slowly in about a week. However, alkyd resin mixtures containing 10 to 40% vernonia oil air-dry at room temperature within several hours.

Clear Coatings. Table 3 compares the properties of 2 mil thick clear coatings obtained under baking conditions in the presence of 0.04 per cent cobalt naphthenate drier at 150°C for one hour on cold rolled steel panels from vernonia oil, pure 10-560 and 10-060 long oil alkyds, and their mixture containing 20 per cent vernonia oil.

All coatings have good adhesion of 4B. Hardness is also good. Pencil hardness is H and Rocker Sward hardness is 42. Both adhesion and hardness improve with higher baking temperature and longer time. Flexibility, according to a standard test by bending the steel panel around 180°, is excellent. We did not observe any cracks or tape-off under the microscope. The impact strength is also excellent. The direct impact strength is 150 pounds.inch; the reverse is 140 pounds.inch.

All three types of coatings have the same properties which indicates that introduction of vernonia oil does not deteriorate the basic properties of alkyd resins.

Long Oil Alkyd Paint Formulations. We also prepared a typical paint based on the formulation shown in Table 1 and compared it with paint formulations in which the initial long oil alkyd was substituted with 20 and 40 per cent vernonia oil. Table 4 compares the Brookfield viscosity (cps.),.RCI drying time (hours) at room temperature, and VOC (lb. per gallon) for coatings 3 mil thick.

The first paint formulation corresponds to the initial formulation based only on alkyd resin (Table 1).

In the second formulation, 20% of the alkyd has been substituted with vernonia oil. Lower viscosity is observed.

The next two formulations still contain 20% vernonia oil but their solvent content has been gradually reduced. The goal is to decrease the solvent to the point at which the viscosity of the paint formulation corresponds to the viscosity of the initial paint formulation without vernonia oil. These two formulations have much lower volatiles.

The fifth formulation is exactly as the first with the only difference being that it contains "our" new, more active CD-44 drier. Drying time of the paint formulations or tack-free time changes very little in the presence of vernonia oil, but sharply decreases in the presence of CD-44.

The last formulation contains the new drier system and 20% of its alkyd resin has been substituted with vernonia oil. The important result here is that by introducing 20% vernonia oil we are able to decrease the volatiles, and thus eventually reduce air-pollution, reduce the drying time, and maintain equal or lower viscosity than the initial paint formulation.

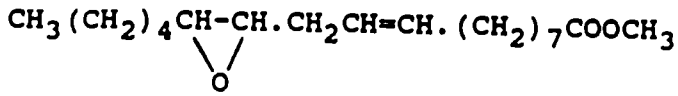
A potential problem for direct application of vernonia oil in alkyd formulations is an anticipated reaction between its epoxy groups and the terminal carboxyl groups of the alkyd resins. Our results show that vernonia oil does not change the can stability of the formulations. Obviously, the epoxy groups of vernonia oil have low reactivity and do not react with the free carboxyl groups of the alkyd resins under test conditions for can stability. The low reactivity of the vernonia oil epoxy groups was confirmed by additional experiments.

Q-UV test, which is a decrease in gloss at 20° and 60° after exposure to UV light and humidity for a week, indicates that vernonia oil improves the coatings weatherability.

Medium Oil Alkyd Paint Formulations. The effect of vernonia oil on paint formulations and coatings based on Reichhold Aroplaz 6440 medium oil alkyd resin is similar to that described above for long oil alkyds.

Epoxy Reactive Diluents. Vernonia oil contains reactive epoxy groups and our initial results show that it is an attractive reactive diluent for epoxy or epoxy ester formulations as well. Another possibility, again for epoxy formulations, is transesterification of vernonia oil with methanol or other higher molecular weight mono-functional alcohols for preparation of very low viscosity diluents.

For example, methyl vernolate shown here has been prepared in quantitative yield:



Similar esters are industrially produced and the U.S. Navy has used them for coatings applications under water. They are very expensive.

Modification of Epoxy Resins and Coatings. The second part of the project is on application of vernonia oil for modification of commercially available epoxy resins and coatings. The project objective is simultaneous improvement of the two main disadvantages of epoxy resins: low toughness and high water absorption.

It is known that a small amount of discrete rubbery particles with an average size of several microns, randomly distributed in a glassy, brittle epoxy resin, dissipates part of the impact energy thus improving crack and impact resistance without deterioration of other properties of the initial epoxy resins.

Epoxy resin toughness is usually achieved by separation of a rubbery phase with a unimodal size distribution from the matrix during the curing process. Different carboxy- or amino-terminated (butadiene, siloxane, etc.) oligomers are used for the formation of the rubbery phase. Some of these oligomers are quite expensive. Vernonia oil, however, opens new opportunities. The epoxy resins based on vernonia oil and commercial amines are elastomers at room temperature. They have low glass transition temperatures, in the range of -80°C to 0°C, which depend on the nature of the diamine used for curing vernonia oil. They appear to be very suitable for toughening of commercial epoxies.

We obtained a two-phase epoxy thermosets and coatings with rubbery vernonia particles by using vernonia liquid rubbers (B-staged materials) as described in the experimental section. For this purpose, vernonia oil was initially B-staged with DDM or 1,12-dodecanediamine. Then homogeneous mixtures of commercial epoxy resin (EPON 825) and commercial amines (DDS, DDM, isophorone diamine, different aliphatic di- and polyamines, etc.), containing 10 to 25 percent vernonia oil B-staged material were cured according to a "standard" curing procedure for epoxy resin. The commercial epoxy resins have higher reactivity with commercial diamines than the epoxy groups of vernonia oil. As a result, they form a rigid matrix at 70°C in which vernonia liquid droplets phase separate. The final

thermoset is cured at 150°C. It consists of a rigid epoxy matrix with randomly distributed small rubbery "vernonia" spherical particles (Figure 3). Diamine molecules on the interface are expected to react with both the epoxy groups of the commercial epoxy resin and the unreacted epoxy groups of vernonia oil, and will presumably form a chemical bonding between the rigid matrix and the rubbery particles.

Several factors control phase separation. Miscibility of the initial mixture of epoxy resin, amine, and vernonia oil or its B-staged material, is required. Incompatibility and phase separation should start during the curing process before gelation for spherical morphology formation. Simultaneously, viscosity at this stage should be high to prevent coalescence and microscopic phase separation. The effective rubbery phase depends on the volume fraction of vernonia oil, nature of curing amine, and time and temperature regime of cure.

The particle diameter is a function of the incompatibility of vernonia B-staged material and the epoxy matrix. We have been able to vary the particle diameter in the range of the desirable particle size for toughening thermosets, e.g. from 0.3 to 50 microns. In general, larger particles are obtained for less compatible systems with more polar diamine, for instance, with DDS for curing the rigid matrix. The electromicrograph of an epoxy thermoset, based on EPON 825, DDM, and 20% of vernonia oil, dodecanediamine B-staged material, shows vernonia rubbery particles with a broad distribution in the range of 5 to 30 microns diameter (Figure 3). The glass transition temperatures of the rubbery phase and the rigid epoxy matrix of this thermoset are observed in DMA at -22° and 160°C, respectively (Figure 4).

Our initial results show improved fracture toughness (K_{IC}), impact resistance and lower water absorption for so modified epoxy resins and coatings. The introduction of vernonia oil into commercial epoxy resins will also result in price reduction. Detailed description of our results is in preparation.

EXPERIMENTAL

Vernonia oil has been kindly supplied by Dr. K. Carlson, U.S. Department of Agriculture. Its extraction from <u>Vernonia galamensis</u> seeds, refining and characterization is described in Ref. 7. The preparation of alkyd coatings formulations is shown in Table 1. The characterization of these formulations and their final coatings has been carried out according to the corresponding ASTMs.

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Two-phase epoxy thermosets and coatings were prepared from vernonia oil which was initially B-staged with amines. A mixture of 100 g of vernonia oil and 25.63 g of 4,4'-methylenedianiline (DDM) was heated at 180oC for 40 hours under nitrogen. Similar results were observed for vernonia B-staged material obtained from 25.9 g of 1,12-dodecanediamine and 100 g of vernonia oil under the same conditions. The vernonia B-staged material based on DDM or 1,12-dodecanediamine was added in 10, 20 or 30 weight percent to a stoichiometric mixture of diglycidyl ether of bisphenol A (Shell epoxy resin EPON 825) and DDM or 4-aminophenyl sulfone (DDS). The resulting DDM homogeneous formulation is additionally B-staged at 75oC for 95 minutes under nitrogen, and then poured into the casting mold and vacuumed. Final cure and post-cure are carried out at 75oC for 4 hours and 150oC for two hours, respectively. The corresponding DDS formulation is B-staged at 150oC for 1 hour under nitrogen and then cured in the mold at 150oC for 2 hours. Both DDM or DDS formulations produce excellent large castings. Electromicrographs were taken by an Amray electron microscope, model 1000B.

CONCLUSION

Vernonia oil, a naturally occuring epoxidized vegetable oil, has a unique structure with reactive epoxy rings, double bonds, lower viscosity than other industrially produced epoxidized vegetable oils, and a low melting point. It is an attractive reactive diluent for preparation of high solids alkyds and epoxy coating formulations.

ACKNOWLEDGMENT

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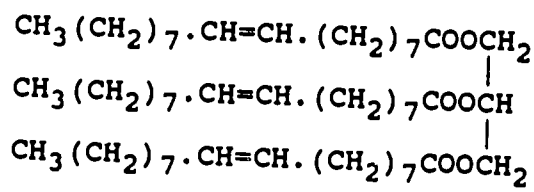
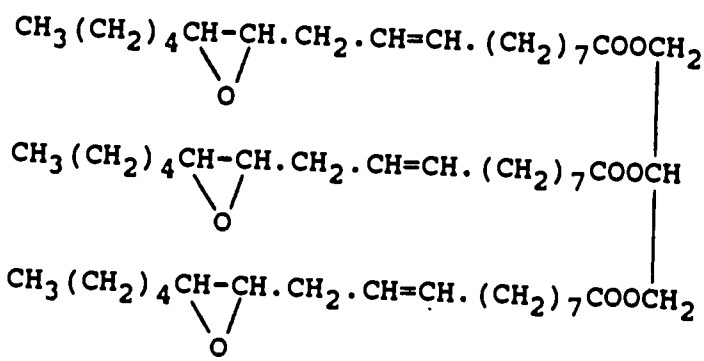
FIGURE 1. MOLECULAR STRUCTURE OF TRIOLEIN, VERNONIA OIL, AND EPOXIDIZED SOYBEAN OIL

TRIOLEIN:



VERNONIA OIL:



EPOXIDIZED SOYBEAN OIL:

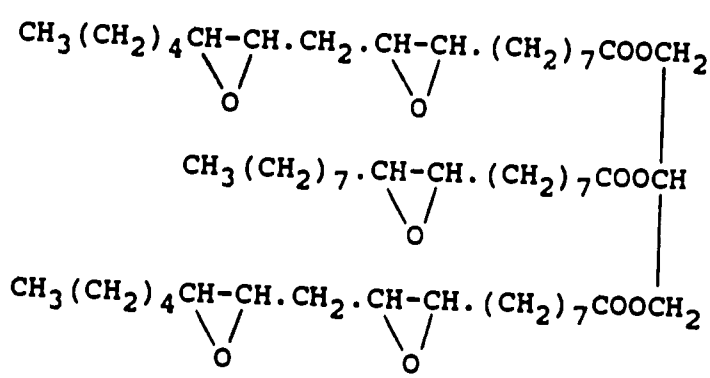


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FIGURE 2. GEL PERMEATION CHROMATOGRAPHY OF VERNONIA OIL (a) AND EPOXIDIZED SOYBEAN OIL (b).

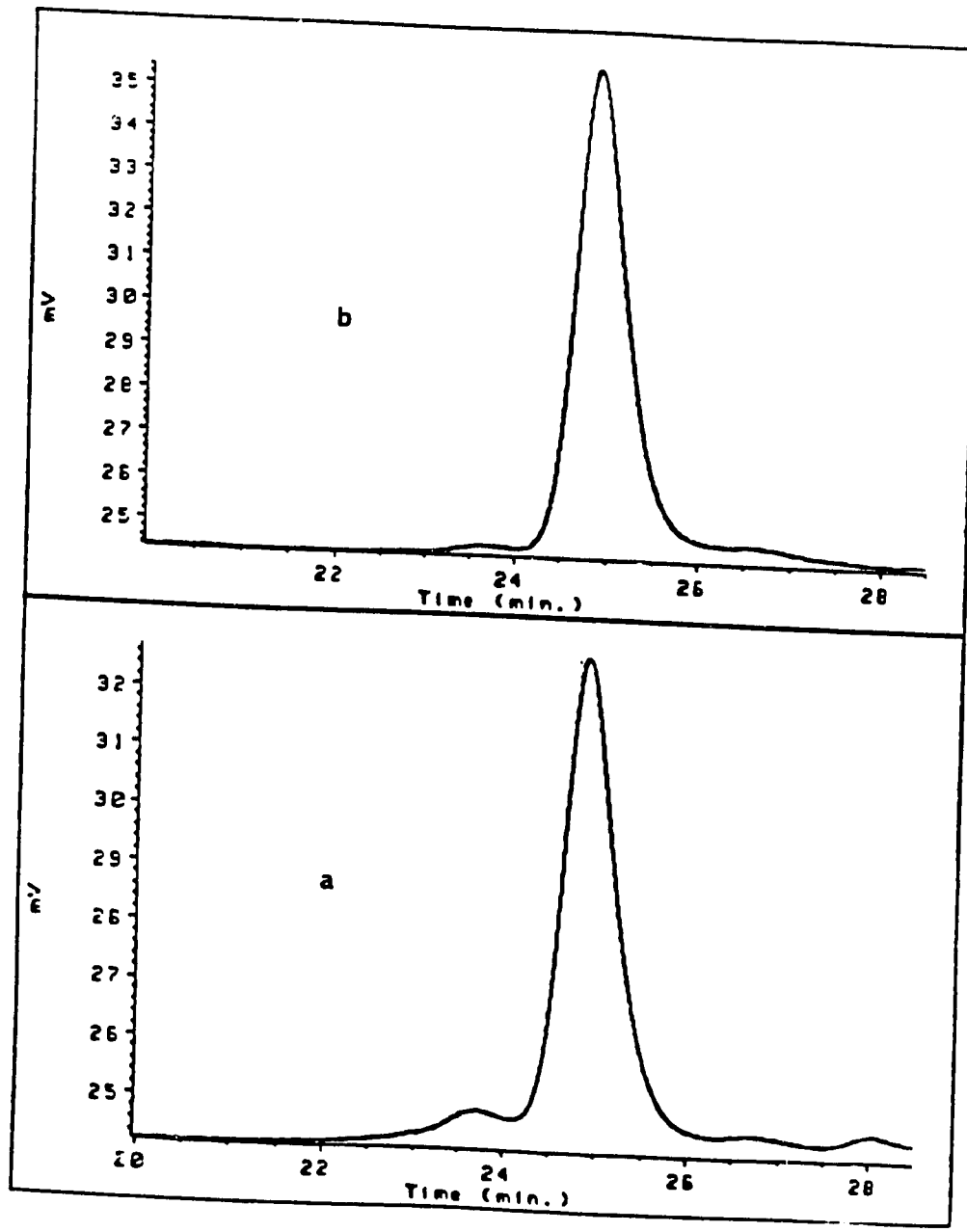

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FIGURE 3. ELECTROMICROGRAPH OF A TWO-PHASE EPOXY RESIN BASED ON EPON 825, DDM, AND 20% VERNONIA/DODECANEDIAMINE LIQUID RUBBER (B-STAGED MATERIAL).

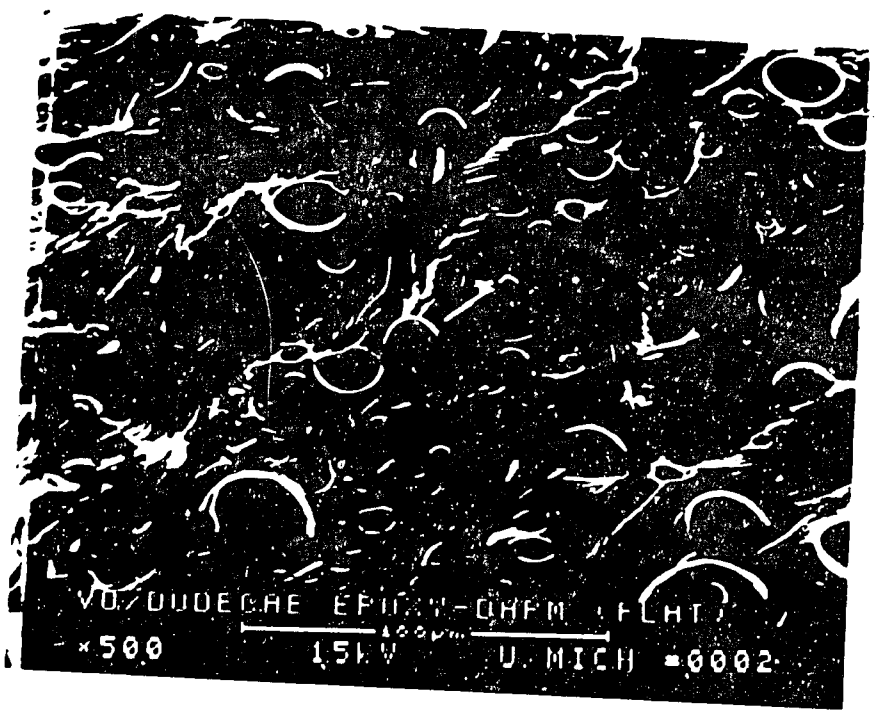

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FIGURE 4. DMA OF TWO-PHASE EPOXY RESIN: MATRIX BASED ON EPON 825 AND DDM (Tg = 160°C) AND RUBBERY PARTICLES (20%) OF VERNONIA OIL AND DODECANEDIAMINE (Tg = -22°C)

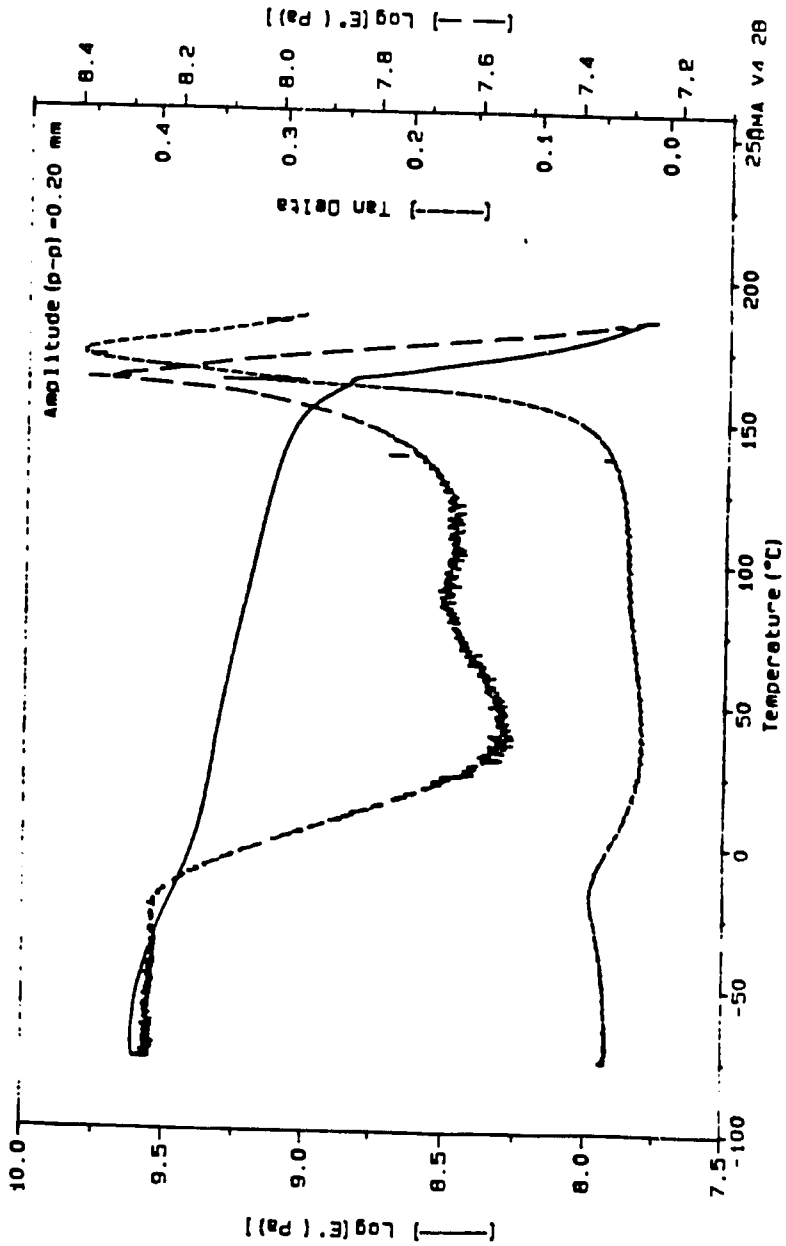

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TABLE 1. COMPOSITION OF PAINT FORMULATIONS BASED ON REICHHOLD BECKOSOL LONG OIL ALKYD 10-060 (WEIGHT PARTS)

10-060 LONG OIL ALKYD (70% SOLIDS)	78.60
ODORLESS MINERAL SPIRITS	23.59
BYK BYKUMEN	3.77
NUODEX NUXTRA CALCIUM 10%	1.12
PREMIX ABOVE	
DUPONT R-900 TiO2	150.97
T & W ATOMITE	37.74
NL CHEMICAL SD-1 BENTONE	2.72
ADD SLOWLY TO COWLS	
10-060 LONG OIL ALKYD	
VERNONIA OIL	81.62
ADD TO GRIND	
NUODEX NUXTRA COBALT 12%	0.46
NUODEX NUXTRA ZIRCO 24%	2.34
ODORLESS MINERAL SPIRITS	93.10
NUODEX EXKIN #2	1.62
PREMIX THEN ADD	

TABLE 2. DRIERS FOR VERNONIA OIL AND ITS MIXTURES WITH ALKYD RESINS

COBALT NAPHTHENATE
ZIRCONIUM DRIER
MANGANESE DRIER
CALCIUM DRIER

DRIER COMBINATIONS:
MOONEY DRIERS: Co, Ca, DRI-Rx
MOONEY DRIERS: Co, Mn, DRI-Rx
NUODEX NUXTRA COBALT
NUODEX NUXTRA ZIRCO
NUODEX NUXTRA CALCIUM
NUODEX ADR
BLENDED METALS/SURFACE DRIER
NUODEX LTD
COMPLEX OF METALS/THROUGH DRIER
NUODEX UTD
COMPLEX OF METALS/THROUGH DRILR
ACTIV 8
DRIER STABILIZER AND ACCELERATOR
MANCHEM MANOSEC CD-44
COBALT DRIER

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TABLE 3. CHARACTERIZATION OF 2 MIL THICK CLEAR COATINGS PREPARED UNDER BAKING CONDITIONS: COBALT DRIER 0.04%, 150°C, 1 HR., ON COLD ROLLED STEEL PANEL

	VERNONIA OIL	ALKYD (80%) VERNONIA OIL (20%)	ALKYD 10-560 10-060
ADHESION	4B	4B	4B
HARDNESS:			
PENCIL	H	2H	H
ROCKER	42	42	46
FLEXIBILITY	EXCELLENT	EXCELLENT	EXCELLENT
IMPACT STRENGTH:			
DIRECT, LB.IN.	150	150	160
REVERSE, LB.IN.	140	140	145

TABLE 4. CHARACTERIZATION OF PAINT FORMULATIONS

	PAINT FORMU-LATION	BROOKFIELD VISCOSITY CPS	RCI DRYING TIME, HR	VOC LB./GAL.
1.	INITIAL 10-060	2640	13	3.15
2.	VO 20%	506	11	3.11
3.	VO 20% LESS SOLVENT	2260	15	2.63
4.	VO 20% LESS SOLVENT	3476	12	2.52
5.	INITIAL 10-060 DRIER CD-44	3344	3-4	2.50
6.	DRIER CE-44 VO 20%	780	4	2.60

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14. S. Dirlikov and I. Frischinger, Toughening of Epoxy Resins with Epoxidized Vegetable Oil, Eastern Michigan University patent disclosure, February 1991.

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RESEARCH CORPORATION TECHNOLOGIES
Invention Disclosure Form

I. Description

Please provide a title for your invention and a brief description. Inventions include new processes, products, apparatus, compositions of matter, living organisms—OR improvements to (or new uses for) things that already exist. Use additional sheets and attach descriptive materials to expand answers to questions. (Sketches, drawings, photos, reports and manuscripts will be helpful.)

A. Invention Title Toughening of Epoxy Resins by Epoxidized Vegetable Oils

B. Description Homogeneous mixtures of commercial epoxy resins, liquid rubbers based on Epoxidized vegetable oils, and amine curing agent form under certain conditions two-phase thermosetting materials which consist of a rigid epoxy matrix and randomly distributed small rubbery particles. These thermosets have better toughness and lower water absorption.

C. What are the immediate and/or future applications of the invention?

Improvement of the two major disadvantages of expoxy resins: low toughness and high water absorption. Several billion pounds of epoxy resins are presently produced with major applications for composites, electronics, coatings, etc.

D. Why is the invention better—more advantageous—than present technology? What are its novel and unusual features? What problems does it solve?

Epoxy toughness is presently achieved by introduction of expensive CTBN oligomers ($2.00-2.50 per pound) into commercial brittle epoxy resins. Epoxidized soybean oil which is available at 50 cents per pound, has better toughening effect, lower sodium content and it is very attractive for large scale commercial applications (See Addendum II.7).

E. Is work on the invention continuing? Are there limitations to be overcome or other tasks to be done prior to practical application? Are there any test data?

Only small scale research continues in order to broaden the scope of the invention. No obstacles anticipated for direct practical applications. Most of the test data are summarized in Addendum II.7.

F. Have products, apparatus or compositions, etc. actually been made and tested?

Yes, see Addendum II, and specially II.7.

II. Publications, Public Use and Sale

Note: valid patent protection depends on accurate answers to the following items.

A. Has invention been disclosed in an abstract, paper, talk, news story or a thesis?

Type of disclosure Yes, see Addendum I, II, and III. (Please enclose a copy) Disclosure Date See Addendum I, II, and III.

II. (Publications, Public Use and Sale—Continued)

B. Is a publication or other disclosure planned in the next six months?

Type of disclosure Yes, see Addendum I and II. Date See Addendum I&II.
(Enclose drafts, abstracts, preprints)

C. Has there been any public use or sale of products embodying the invention?

Describe, giving dates None

D. Are you aware of related developments by others? If "yes," please give citations. Copies of any relevant patents or publications would be appreciated.

None

III. Sponsorship

If the research that led to the invention was sponsored, please fill in the details and attach a copy of the contract or agreement if possible.

A. Government agency U.S. Agency for International Development contract/grant no. 9.035

B. Name of industry, university, foundation or other sponsor:

South Coast Air Quality Management District

C. Has the invention been disclosed to industry representatives? If "yes," please provide details, including the names of companies and their representatives.

Yes, see Addendum

IV. For Our Records

A. Names and titles of inventors (please print; sign where indicated)

1. Isabelle Frischinger Signature I. Frischinger Date February 4, 1991
2. Stoil Dirlikov Signature Stoil Dirlikov Date February 4, 1991
3. Signature Date

B. Contact for more data Stoil Dirlikov Tel. (313) 487-1161

C. Mailing address for inventor(s) Coatings Research Institute, 122 Sill Hall, Eastern Michigan University, Ypsilanti, MI 48197

D. Name and title of institutional representative (please sign where indicated)

Dr. David Clifford Signature Date

Department Office of Research Development Tel. (313) 487-0090

Mailing address B-18 Goddard Hall, Eastern Michigan University, Ypsilanti, MI 48197

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I. **Presentations** (without publications)

1. I. Frischinger, S. Dirlikov (invited participant) and R. Pearson; "Toughening of Epoxy Resins with Epoxidized Vegetable Oils" poster session, Florida Advanced Materials Chemistry Conference, Palm Coast Resort, Florida, June 1990.

2. I. Frischinger, S. Dirlikov (invited participants) and R. Pearson; Toughening of Epoxy Resins with Epoxidized Vegetable Oils, poster session, Gordon Research Conference on Thermosetting Polymers, Colby-Sawyer College, New London, NH, June 1990.

3. S. Dirlikov (invited speaker), New Reactive Diluents for High Solids Coatings, Aqualon-Hercules Research Center, Wilmington, DE, August 1990.

4. S. Dirlikov (invited speaker), New Reactive Diluents for High Solids Coatings, Rohm & Haas Research Center, Spring House, PA, August 1990.

5. S. Dirlikov (invited speaker), New Reactive Diluents for High Solids Coatings, Paint Research Associates, Detroit, MI September 1990.

6. S. Dirlikov (invited speaker), Vernonia Oil: A New Reactive Diluent, Howard University, Washington, DC, October 1990.

7. S. Dirlikov (invited speaker), New Reactive Diluents for Reactive Coatings, First North American Research Conference on Organic Coatings: Science and Technology, Hilton Head, SC, December 1990.

8. S. Dirlikov (invited speaker), M.S. Islam, I. Frischinger, D. Wang, T. Lepkowski, and P. Muturi, Vernonia Oil: A New Reactive Diluent for High Solids Alkyd and Epoxy Resins and Coatings, San Diego, CA, May 1991 (in preparation).

9. S. Dirlikov (invited speaker), New Reactive Diluents for Alkyds and Epoxies, Engineering Society of Detroit and American Society of Manufacturers, Coatings Technology Conference, Dearborn, MI, June 1991.

II. **Published Abstracts, Papers, and Book Chapters** (copies included)

1. S. Dirlikov, I. Frischinger, M. Safiqul Islam, J. Graham, Vernonia Oil: A New Reactive Monomer, 199th ACS Meeting, Boston, MA, April 1990. Proceedings of the ACS Division of Polymeric Materials: Science and Engineering, 62, 217 (1990).

2. I. Frischinger, S. Dirlikov, Y. Feng and R. Pearson; Toughening of Epoxy and Propargyl Terminated Resins, 200th ACS Meeting, PMSE Division, Washington, DC, August 1990, abstract PMSE 130. Proceedings of the ACS Division of Polymeric Materials: Science and Engineering, 63, 588 (1990).

3. S. Dirlikov, I. Frischinger and M.S. Islam; Application of Vegetable Oils in Polymer Chemistry, 200th ACS Meeting, CELL Division, Washington, DC, August 1990, abstract: CELL 18.

4. S. Dirlikov, M.S. Islam, I. Frischinger, T. Lepkowski, and P. Muturi, Vernonia Oil: A New Reactive Diluent for Alkyd and Epoxy Resins and Coatings, European Polymers Paint Colour Journal, 666, November 1990.

5. S. Dirlikov, M.S. Islam, I. Frischinger, T. Lepkowski, and P. Muturi, Vernonia Oil: A New Reactive Diluent for High Solids Alkyd and Epoxy Resins and Coatings, 18th Annual Waterborne, Higher-Solids, and Powder Coatings Symposium, New Orleans, LA, February 1991.

6. S.K. Dirlikov, I. Frischinger, M.S. Islam and T.J. Lepkowski; Vernonia Oil: A New Reactive Monomer, Chapter in ACS Symposium Series Book "Polymers from Biotechnology", C.G. Gebelein, Ed., Plenum Press, 1991 (in press).

7. I. Frischinger and S. Dirlikov; Toughening of Epoxy Resins by Epoxidized Soybean Oil, Chapter in Advances in Chemistry" Series, American Chemical Society, on "Toughened Plastics" (submitted).

III. News Story

1. Chemical Engineering News, pp. 62, May 7, 1990.

2. INFORM, 1, May 1990, pp. 440.

3. Chemical Engineering News, pp. 22, September 10, 1990.

15. I Frischinger, S. Dirlikov, Toughening of Epoxy Resins by Epoxidized Vegetable Oils, POLYMER (in press).

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Eastern Michigan University
Ypsilanti, Michigan 48197

September 13, 1991

Mrs. Sue Bourner
Editor/Executive Editor
Butterworth-Heinemann Ltd
Linacre House
Jordan Hill
Oxford
OX2 8DP, UK.

Dear Mrs. Bourner:

Thank you for your letter and enclosed proofs of our article (APC 329) which we received two days ago, September 11, 1991.

Enclosed is one copy of the proofs with our corrections. I will ask you to include an acknowledgement part at the end of the article if possible:

ACKNOWLEDGEMENT

The authors thank USAID and SCAQMD for their financial support.

This acknowledgement has been omitted in our original manuscript because of POLYMER "1000 Words" manuscript limitation for Letters preparation. The proofs indicate that there might be enough space for it.

Thanking you in advance.

Sincerely,

Stoil Dirlikov, Ph.D.
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Toughening of epoxy resins by epoxidized vegetable oils

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(Received 8 March 1991; revised 21 June 1991)

Homogeneous mixtures of a liquid rubber, based on prepolymers of epoxidized vegetable oils with amines, diglycidyl ether of bisphenol A (DGEBA) epoxy resins and commercial diamines form, under certain conditions, two-phase thermosetting materials which consist of a rigid DGEBA epoxy matrix and randomly distributed small 'vegetable' rubbery particles.

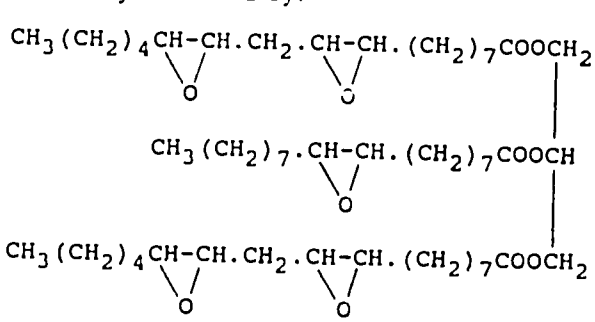
(Keywords: two-phase thermosets; commercial epoxy resins; epoxidized vegetable oils; epoxidized soybean oil; rubber toughening)

It is well established that a small amount of discrete rubbery particles with an average size of several micrometres randomly distributed in a glassy, brittle epoxy thermoset, dissipates part of the impact energy, thus improving crack and impact resistance without major deterioration of other properties of the unmodified epoxy thermosets[1,2].

The epoxy toughness is usually achieved by separation of a rubbery phase with a unimodal size distribution from the matrix during the curing process. Different reactive liquid rubbers, based on low molecular carboxy- or amino-terminated oligomers of butadiene and acrylonitrile (CTBN and ATBN), are usually used for the formation of the rubbery phase. Low molecular weight amino-terminated (methyl)siloxanes offer other alternatives. However, some of these oligomers are quite expensive.

Epoxidized vegetable oils such as vernonia, epoxidized soybean (ESO) and linseed oils provide new opportunities. Their epoxy resins with commercial diamines are elastomers at room temperature with low glass transition temperatures (T_gs) in the range of -70 to $0°C$, depending on the nature of the amine used for curing.

Epoxidized vegetable oils consist of a mixture of different triglycerides. The ESO molecular structure is schematically illustrated by:



The commercial epoxy resin used in the present study is EPON 825 which is practically pure diglycidyl ether of bisphenol A (DGEBA). Most of the research has been done with its stoichiometric 4,4'-diaminodiphenylmethane (DDM) or 4,4'-diaminodiphenyl sulphone (DDS) formulations. Only initial screening evaluation has been carried out on DGEBA formulations with other cycloaliphatic (isophorone diamine) and aliphatic diamines and polyamines (1,10-decanediamine, 1,12-dodecanediamine, diethylenetriamine, triethylenetetramine, etc.). These epoxy/amine formulations were toughened by the addition of 10, 15, 20 and 30% of epoxidized vegetable oil or liquid rubber (prepolymer) as described below.

Our initial attempts for toughening epoxy resins were carried out directly with epoxidized vegetable oils. For this purpose, homogeneous mixtures of DGEBA, diamine and epoxidized vegetable oil at a stoichiometric epoxy/amine ratio (1:1) were cured according to a 'conventional' curing procedure for epoxy resin at 70°C. The diamines have a much higher reactivity with DGEBA than with the epoxy groups of the epoxidized vegetable oil. As a result, they form a rigid matrix at 70°C in which the epoxidized oil separates as a second phase of small liquid droplets. Unfortunately, at a higher temperature of 150°C these liquid droplets do not cure with the remaining diamine fast enough to form rubbery particles and we have not been able to prepare two-phase thermosets. Instead, the epoxidized vegetable oils dissolve and plasticize the rigid DGEBA matrix. One-phase homogeneous thermosets with single lower T_gs are obtained as observed by scanning electron microscopy and differential scanning calorimetry respectively.

We were able to obtain two-phase thermosets with rubbery 'vegetable' particles under the same curing conditions by using epoxidized vegetable liquid rubber instead of the initial pure epoxidized vegetable oil. These liquid rubbers were prepared by B-staging (prepolymerization) of a stoichiometric mixture of epoxidized vegetable oil and DDM (or 1,12-diaminododecane) at temperatures ranging from 135 to 180°C for ~40 h. They contain oligomers with a broad molecular weight distribution in addition to a small amount of the unreacted initial epoxidized vegetable oil.

The 'vegetable' particles again separated from the initial homogeneous mixture of DGEBA, diamine and epoxidized vegetable liquid rubber. The higher molecular weight of the liquid rubber (in comparison to that of the initial epoxidized oil) increases its incompatibility with

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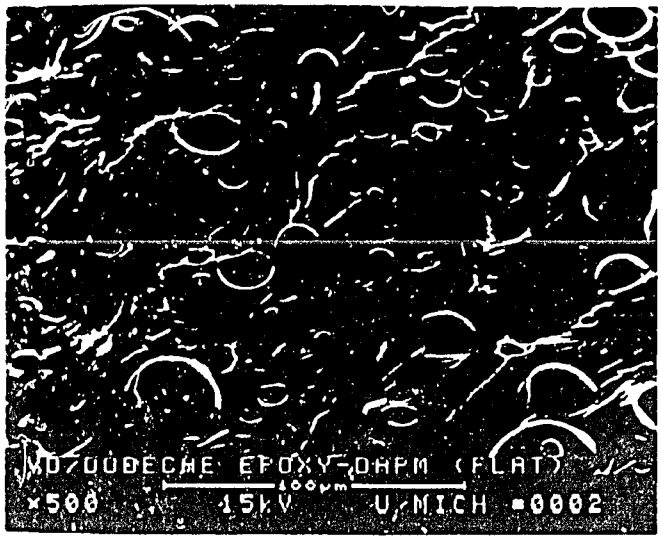

Figure 1 SEM micrograph of the fracture surface of a two-phase thermoset which consists of a DGEBA/DDM rigid matrix and rubbery particles based on vernonia oil/1,12-dodecanediamine liquid rubber (20%)

Figure 2 SEM micrograph of the fracture surface of a two-phase thermoset which consists of a DGEBA/DDS rigid matrix and rubbery particles based on epoxidized soybean oil/DDM liquid rubber (20%)

the epoxy matrix at higher temperature. As a result, the final thermoset, after being cured at 150°C, consists of a rigid epoxy matrix with randomly distributed small 'vegetable' rubbery spherical particles (*Figures 1* and *2*). The diamine molecules on the interface are expected to react with both the epoxy groups of the commercial epoxy resin and the unreacted epoxy groups of the epoxidized vegetable rubber, and to form chemical bonds between the rigid matrix and the rubbery particles.

Table 1 Glass transition temperature, T_g, of the rigid DGEBA matrix[a], stress intensity factor, K_{IC}, fracture energy, G_{IC}, and Young's modulus, E, of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR, DGEBA/DDS/ESR and DGEBA/DDS/CTBN formulations

Thermoset formulation	T_g (°C)	K_{IC} (MPa m$^{1/2}$)	G_{IC} (J m^{-2})	E (MPa)
DGEBA/DDM	190	0.75	175	2840
DGEBA/DDM/ESR-10[b]	–	–	–	–
DGEBA/DDM/ESR-15	161	1.24	564	2410
DGEBA/DDM/ESR-20	165	1.33	802	1950
DGEBA/DDM/ESR-30	145	1.40	1008	1720
DGEBA/DDS	185	0.75	145	3420
DGEBA/DDS/ESR-10	168	1.09	374	2810
DGEBA/DDS/ESR-20	166	1.19	596	2100
DGEBA/DDS/ESR-30[c]	161	0.54	145	1780
DGEBA/DDS[d]	–	–	162	3360
DGEBA/DDS/CTBN-10[d]	–	–	242	3000

[a] T_g of the rubbery ESR particles is in the range of −30 to −45°C
[b] This formulation does not phase separate and its properties have not been determined
[c] SEM shows that this formulation undergoes phase inversion at 30% ESR. Larger rubbery particles (100–200 µm) containing small rigid particles (several µm) are observed in the rigid matrix. Obviously, the phase inversion phenomenon lowers the fracture toughness
[d] Literature data[3] for comparison of the ESR and CTBN effects on DGEBA/DDS formulations

Particle size varies in the range from 0.1 to 5 µm and depends on the nature, volume fraction, and degree of prepolymerization of the epoxidized vegetable oil, nature of diamine, kinetics of curing, etc. The phase inversion phenomenon is observed at ~30% 'vegetable' content.

Most of the research has been carried out with epoxidized soybean liquid rubber (ESR) based on epoxidized soybean oil and DDM. Initial unoptimized results show that these ESR two-phase thermosets have better toughness, similar to that of other rubber-modified (CTBN) epoxies (*Table 1*), lower water absorption and low sodium content. They exhibit slightly lower T_gs and Young's moduli in comparison to the unmodified thermosets (*Table 1*), whereas their dielectric properties do not change. The epoxidized soybean oil is cheaper than commercial epoxy resins and CTBN and appears very attractive for epoxy toughening on an industrial scale. Further research is in progress.

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1 Riew, K. C. (Ed.) *Adv. Chem. Ser.* no. 222, 1989
2 Riew, K. C. and Gillham, J. K. (Eds) *Adv. Chem. Ser.* no. 208, 1984
3 Pearson, R. A. and Yee, A. F. *J. Mater. Sci.* 1989, 24, 2571

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ACKNOWLEDGEMENT

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The authors thank USAID and SCAQMD for their financial support.

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16. S. Dirlikov, 1991 Midwest Industrial Uses Conference "Agricultrual Resources in Industry - Biotech Product and Business Opportunities for the 90s", Michigan Molecular Institute, East Lansing, MI, May 1991.

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SOCIETY FOR THE ADVANCEMENT OF MATERIAL AND PROCESS ENGINEERING

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VOLUME 1

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Edited by
Gil Carrillo
Earl Newell
Gary Serio

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May 21-23, 1991

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LOW VOC COATINGS BASED ON VERNONIA OIL REACTIVE DILUENTS

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ABSTRACT

Vernonia oil has been evaluated for preparation of high solids coatings formulations by replacing conventional solvents. Vernonia oil is a natural epoxidized vegetable oil at a developmental stage in several countries. Trivernolin, the principal triglyceride, has a unique structure with three reactive epoxy groups and three carbon-carbon double bonds per molecule. Vernonia oil is characterized by very low viscosity, lower m.p., homogeneous molecular structure and potentially low price. It appears to be an attractive reactive diluent for low VOC alkyd and epoxy resins and coatings applications.

KEYWORDS: Low VOC; Alkyd Coatings; Epoxy Resins; Vernonia Oil; Reactive Diluents.

1. INTRODUCTION

The South Coast Air Basin (Orange, and non-desert parts of Los Angeles, San Bernardino, and Riverside Counties) frequently has unhealthful levels of ozone and PM_{10},

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exceeding both federal and California standards. For example, monitored ozone levels are nearly three times the national standard and PM_{10} levels are nearly twice the national average. A recent air quality analysis developed by the South Coast Air Quality Management District provides perspective to the magnitude of the problem and the need for additional VOC controls. The analysis indicates that an additional 75 to 80 percent reduction in VOC emissions will be needed to achieve all standards, and that such a reduction will necessitate the implementation of all known controls as well as the development of new control approaches for future implementation. Without these control strategies, the high ozone levels will continue to occur.

The federal (and California) PM_{10} standards and the California visibility standard are also exceeded by a wide margin within the region. These exceedances are also related to VOC emissions, but to a lesser degree. VOCs consist primarily of hydrocarbons. VOC emissions react with other pollutants in the presence of sunlight to form photochemical oxidants, most notably ozone. Atmospheric hydrocarbon concentrations are generally higher in winter because these reactive hydrocarbons react more slowly and meteorological conditions are more favorable for their accumulation to higher concentrations before producing photochemical oxidants. Thus, VOC emissions also contribute to PM_{10} and poor visibility.

Although the specific health effects of some of the gaseous hydrocarbon components of VOC emissions in ambient air has not been demonstrated, health impacts are know to occur at high concentration (1000 ppm or greater), because of interference with oxygen uptake. In general, these hydrocarbons in the atmosphere are suspected to cause coughing, sneezing, headaches, nervous weakness, laryngitis, and bronchitis, even at low concentrations. The effect of these hydrocarbon components of VOC emissions are thought or are known to be hazardous. For example, benzene, one hydrocarbon component of VOC emissions, is a known human carcinogen. Hematologic effects have been reported from repeated exposure to concentrations as low as 66 ppm.

Reduction of VOC emissions is part of the District's long range strategy to attain the ozone standard. The District has identified a combination of VOC emissions reduction strategies which must be implemented in the "near future".

The South Coast Air Quality Management District (SCAQMD) Board recognized that the Basin's air quality problem cannot be solved by controlling any one category of sources and that advanced technologies would be required to control emission on all stationary and mobile sources. With this need in mind, and to meet the alternative fuel and low-emission technology goals of the AQMD, the District Board created the Technology Advancement Office (TAO). On January 8, 1988, the District Board adopted a five-year, $30.4 million Clean Fuels Program, to be implemented by the TAO. The primary objective of the Clean Fuels Program is to

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support and facilitate the goals of the AQMD for the use of alternative fuels in both the mobile and stationary sources sectors. The TAO is also charged with identifying technologies from anywhere in the world which may have application in cleaning up the emission in the Los Angeles area. Programs have been established to address reduction in solvents emissions from coatings, NOx emissions, and other technologies such as advanced combustion modification and the use of solar energy.

The SCAQMD announced new regulations for the reduction of hydrocarbon emissions by 80 to 90% over the next 5 years. This means reducing total emissions for paint and varnishes from 22.1 tons a day to just 2.9 tons a day - a requirement that would be all but impossible with today's technologies. To foster new technology, the TAO has formed a strategy to aid paint and varnish makers in developing new coatings that do not emit hydrocarbons in the first place. Initial (unreacted) vernonia oil has a VOC content of less than 3 g/l. The use of vernonia oil as a reactive diluent for alkyd and epoxy resins and coatings appears to hold much promise for new low VOC paint and varnish formulation.

2. EXPERIMENTAL

Vernonia oil has been kindly supplied by Dr. K. Carlson, U.S. Department of Agriculture. Its extraction from Vernonia galamensis seeds, refining and characterization is described in Ref. 7. The preparation of alkyd coatings formulations is shown in Table 1. The characterization of these formulations and their final coatings has been carried out according to the corresponding ASTMs.

Two-phase epoxy thermosets and coatings were prepared from vernonia oil which was initially B-staged with amines. A mixture of 100 g of vernonia oil and 25.63 g of 4,4'-methylenedianiline (DDM) was heated at 180°C for 40 hours under nitrogen. Similar results were observed for vernonia B-staged material obtained from 25.9 g of 1,12-dodecanediamine and 100 g of vernonia oil under the same conditions. The vernonia B-staged material based on DDM or 1,12-dodecanediamine was added in 10, 20 or 30 weight percent to a stoichiometric mixture of diglycidyl ether of bisphenol A (Shell epoxy resin EPON 825) and DDM or 4-aminophenyl sulfone (DDS). The resulting DDM homogeneous formulation is additionally B-staged at 75°C for 95 minutes under nitrogen, and then poured into the casting mold and vacuumed. Final cure and post-cure are carried out at 75°C for 4 hours and 150°C for two hours, respectively. The .h1 4 corresponding DDS formulation is B-staged at 150°C for 1 hour under nitrogen and then cured in the mold at 150°C for 2 hours. Both DDM or DDS formulations produce excellent .h1 6large castings. Electromicrographs were taken by an Amray electron microscope, model 1000B.

3. VERNONIA GALAMENSIS

Vernonia galamensis, the source of vernonia oil, is a new

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potential oil seed crop for frost-free areas (1-6). Some varieties grow in arid and semi-arid areas of the tropics and sub-tropics on land that is unsuitable for food crops. It is an annual weed. It has good seed retention and seeds germinate easily. It also has natural resistance to disease, nematodes, and most insects. Neither wild nor domestic animals consume Vernonia galamensis.

"Vernonia" seeds contain about 42% oil in contrast to soybeans, which contain only 17% oil. The maximum seed yield reached at this development stage is 1009 kg (2227 pounds) per acre which compares favorably with an average yield of 872 kg (1,926 pounds) per acre for soybeans in the U.S. in 1979, the best yield for this crop in the U.S. from 1971 through 1984 (2). Increased yields of vernonia seed are expected by breeding as greater genetic diversity becomes available.

In summary, it appears that the major agronomic problems for cultivation have been resolved. This new crop is currently at a developmental stage in several African countries, especially in Zimbabwe and Kenya and it has the potential to become a major industrial crop. Several major chemical and coatings companies have expressed strong interest in vernonia oil. Rhône-Poulenc (U.S.A. division) has started experimental crop trials for vernonia oil production, and several tons of Vernonia galamensis seeds are being harvested this year. Cargill is evaluating the possibilities for cultivation of Vernonia galamensis and the potential use of vernonia oil as well.

4. RESULTS AND DISCUSSION

4.1 Properties of Vernonia Oil. Vernonia oil has several unique features:

a. It is a transparent homogeneous liquid at room temperatue with excellent solubility in many organic solvents, diluents, and paints.

b. Vernonia oil has a low viscosity of 300 cps (30 Pa.s) at 10°C (50°F) and 100 cps (10 Pa.s) at 30.5°C (85°F).

c. It has a low melting point of 2°C (-36°F).

d. Vernonia oil has a homogeneous molecular structure consisting predominantly of identical triglyceride molecules which have three equal vernolic acid residues. In contrast, all other vegetable oils consist of a heterogeneous mixture of triglycerides with different fatty acid residues.

e. It is expected to be available at a low price in the range of $1.00-1.50 per pound (1 pound = 453 g).

f. Toxicity of vernonia oil is expected to correspond to that of the epoxidized soybean and linseed oils which are industrially produced.

4.2 Vernonia vs. Other Epoxidized Vegetable Oils. We believe that vernonia oil does not compete with other epoxidized vegetable oils, i.e. epoxidized soybean oil and epoxidized linseed oil, which are industrially produced by epoxidation of unsaturated vegetable oils and have structures similar to vernonia oil. Epoxidized soybean and linseed oils are less suitable for coatings applications as reactive diluents because of their higher viscosity.

Both epoxidized soybean oil and linseed oils have higher viscosity, i.e. in the range of 1000 - 2000 cps (100 - 200 Pa.s) at 10°C (50°F), in contrast to 300 cps (30 Pa.s) for vernonia oil. Both are heterogeneous semi-solids even at 24°C (75°F) and form homogeneous, clear liquids only above 30.5°C (85°F). Their applications require a warming procedure at 49°C (120°F) with mild agitation prior to use for at least one hour.

The difference in viscosity of vernonia oil and epoxidized soybean oil is rather surprising since both have similar molecular structures. Initially, we thought that soybean oil partially polymerizes during the epoxidation reaction and the resulting epoxidized soybean oil contains a certain amount of oligomers which increases its viscosity. GPC of vernonia oil and epoxidized soybean oil, however are identical (Figure 2). Evidently, both oils have exactly the same molecular weight distribution and the low viscosity is an inherent characteristic of vernonia oil.

4.3 Drying Mechanism of Vernonia Oil. Carlson and co-workers (7) have reported that "vernonia" coatings can be obtained directly from vernonia oil by a standard baking procedure at 150°C for 30 minutes in the presence of different drier systems.

We were interested in the drying mechanism of vernonia oil since it has two functionalities: unsaturated double bond and epoxy ring. For this purpose, we have compared the drying characteristics of triolein, vernonia oil, and epoxidized soybean oil in the presence of 0.5 per cent cobalt drier under baking conditions at 150°C for one hour. The molecular structure of these three oils is shown in Figure 1.

Epoxidized soybean oil does not form coatings at 185°C for several hours. Obviously, its epoxy groups do not polymerize under these conditions.

Both triolein and vernonia oil form good coatings. These results show that vernonia oil drying is based on its unsaturated carbon-carbon double bonds and not on its epoxy functionality. This allows its application as a reactive diluent, not only in epoxy and epoxy-ester formulations, but in alkyd resins as well.

Results also show that vernonia oil dries at lower temperature and much faster than triolein. Good coatings

have been obtained from vernonia oil at 150°C for half an hour. Triolein does not form coatings at 150°C for 1 hour. It forms coatings only at 180°C for 1.5 hours. The epoxy rings of vernonia oil probably activate the oxidation of the methylene group between the epoxy ring and the carbon-carbon double bond and therefore dries faster than triolein.

4.4 Compatibility with Alkyd Resins. We carried out compatibility studies with Reichhold Beckosol long oil alkyds 10-560 and 10-060, medium oil alkyd 11-035, and short oil alkyd 12-005. Vernonia oil is compatible with all three types of alkyd resins at any ratio.

4.5 Drier Evaluation. We evaluated different driers and drier combinations for vernonia oil and for its 20% mixtures in alkyd resins (Table 2). Cobalt drier at 0.1 per cent concentration forms good coatings at 150°C for 1 hr. Zirconium drier does not form coatings even at higher concentration (0.5%), higher temperature (160°C) and longer time (2 hours). Calcium and manganese driers have intermediate activity, weaker than the cobalt drier but stronger than the zirconium. Without going into further detail, Manchem Manosec CD-44 drier gives the best results. It is more active than all other driers and drier combinations. It contains cobalt (0.6%), calcium (0.2%), and lithium (0.03%) carboxylates in mineral spirits.

Vernonia oil does not air dry with none of the driers at room temperature for several hours. In the presence of Manosec CD-44 it dries slowly in about a week. However, alkyd resin mixtures containing 10 to 40% vernonia oil air-dry at room temperature within several hours.

4.6 Clear Coatings. Table 3 compares the properties of 2 mil (52 microns) thick clear coatings obtained under baking conditions in the presence of 0.04 per cent cobalt naphthenate drier at 150°C for one hour on cold rolled steel panels from vernonia oil, pure 10-560 and 10-060 long oil alkyds, and their mixture containing 20 per cent vernonia oil.

All coatings have good adhesion of 4B. Hardness is also good. Pencil hardness is H and Rocker Sward hardness is 42. Both adhesion and hardness improve with higher baking temperature and longer time. Flexibility, according to a standard test by bending the steel panel around 180°C, is excellent. We did not observe any cracks or tape-off under the microscope. The impact strength is also excellent. The direct impact strength is 150 ft.pounds/inch; the reverse is 140 ft.pounds/inch (0.0534 ft lb/in = 1kJ/m).

All three types of coatings have the same properties which indicates that introduction of vernonia oil does not deteriorate the basic properties of alkyd resins.

4.7 Long Oil Alkyd Paint Formulations. We also prepared a typical paint based on the formulation shown in Table 1 and compared it with paint formulations in which the initial

long oil alkyd was substituted with 20 and 40 per cent vernonia oil. Table 4 compares the Brookfield viscosity (cps.), RCI drying time (hours) at room temperature, and VOC (lb. per gallon) for coatings 3 mil (78 microns) thick.

The first paint formulation corresponds to the initial formulation based only on alkyd resin (Table 1).

In the second formulation, 20% of the alkyd has been substituted with vernonia oil. Lower viscosity is observed.

The next two formulations still contain 20% vernonia oil but their solvent content has been gradually reduced. The goal is to decrease the solvent to the point at which the viscosity of the paint formulation corresponds to the viscosity of the initial paint formulation without vernonia oil. These two formulations have much lower volatiles.

The fifth formulation is exactly as the first with the only difference being that it contains "our" new, more active CD-44 drier. Drying time of the paint formulations or tack-free time changes very little in the presence of vernonia oil, but sharply decreases in the presence of CD-44.

The last formulation contains the new drier system and 20% of its alkyd resin has been substituted with vernonia oil. The important result here is that by introducing 20% vernonia oil we are able to decrease the volatiles, and thus eventually reduce air-pollution, reduce the drying time, and maintain equal or lower viscosity than the initial paint formulation.

A potential problem for direct application of vernonia oil in alkyd formulations is an anticipated reaction between its epoxy groups and the terminal carboxyl groups of the alkyd resins. Our results show that vernonia oil does not change the can stability of the formulations. Obviously, the epoxy groups of vernonia oil have low reactivity and do not react with the free carboxyl groups of the alkyd resins under test conditions for can stability. The low reactivity of the vernonia oil epoxy groups was confirmed by additional experiments.

Q-UV test, which is a decrease in gloss at 20° and 60° after exposure to UV light and humidity for a week, indicates that vernonia oil improves the coatings weatherability.

4.8 Medium Oil Alkyd Paint Formulations. The effect of vernonia oil on paint formulations and coatings based on Reichhold Aroplaz 6440 medium oil alkyd resin is similar to that described above for long oil alkyds.

4.9 Epoxy Reactive Diluents. Vernonia oil contains reactive epoxy groups and our initial results show that it is an attractive reactive diluent for epoxy or epoxy ester formulations as well. Another possibility, again for epoxy formulations, is transesterification of vernonia oil with methanol or other higher molecular weight mono-functional

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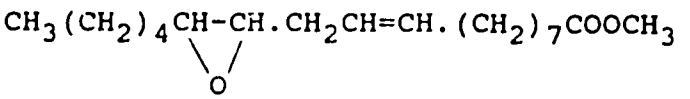
alcohols for preparation of very low viscosity diluents. For example, methyl vernolate shown here has been prepared in quantitative yield:



Similar esters are industrially produced and the U.S. Navy has used them for coatings applications under water. They are very expensive.

4.10 Modification of Epoxy Resins and Coatings. The second part of the project is on application of vernonia oil for modification of commercially available epoxy resins and coatings. The project objective is simultaneous improvement of the two main disadvantages of epoxy resins: low toughness and high water absorption.

It is known that a small amount of discrete rubbery particles with an average size of several microns, randomly distributed in a glassy, brittle epoxy resin, dissipates part of the impact energy thus improving crack and impact resistance without deterioration of other properties of the initial epoxy resins.

Epoxy resin toughness is usually achieved by separation of a rubbery phase with a unimodal size distribution from the matrix during the curing process. Different carboxy- or amino-terminated (butadiene, siloxane, etc.) oligomers are used for the formation of the rubbery phase. Some of these oligomers are quite expensive. Vernonia oil, however, opens new opportunities. The epoxy resins based on vernonia oil and commercial amines are elastomers at room temperature. They have low glass transition temperatures, in the range of -80°C to 0°C, which depend on the nature of the diamine used for curing vernonia oil. They appear to be very suitable for toughening of commercial epoxies.

We obtained a two-phase epoxy thermosets and coatings with rubbery vernonia particles by using vernonia liquid rubbers (B-staged materials) as described in the experimental section. For this purpose, vernonia oil was initially B-staged with DDM or 1,12-dodecanediamine. Then homogeneous amines (DDS, DDM, isophorone diamine, different aliphatic di- and polyamines, etc.), containing 10 to 25 percent vernonia oil B-staged material were cured according to a "standard" curing procedure for epoxy resin. The commercial epoxy resins have higher reactivity with commercial diamines than the epoxy groups of vernonia oil. As a result, they form a rigid matrix at 70°C in which vernonia liquid droplets phase separate. The final thermoset is cured at 150°C. It consists of a rigid epoxy matrix with randomly distributed small rubbery "vernonia" spherical particles (Figure 3). Diamine molecules on the interface are expected to react with both the epoxy groups of the commercial epoxy resin and the unreacted epoxy groups of vernonia oil, and will presumably form a chemical bonding between the rigid

matrix and the rubbery particles.

Several factors control phase separation. Miscibility of the initial mixture of epoxy resin, amine, and vernonia oil or its B-staged material, is required. Incompatibility and phase separation should start during the curing process before gelation for spherical morphology formation. Simultaneously, viscosity at this stage should be high to prevent coalescence and microscopic phase separation. The effective rubbery phase depends on the volume fraction of vernonia oil, nature of curing amine, and time and temperature regime of cure.

The particle diameter is a function of the incompatibility of vernonia B-staged material and the epoxy matrix. We have been able to vary the particle diameter in the range of the desirable particle size for toughening thermosets, e.g. from 0.3 to 50 microns. In general, larger particles are obtained for less compatible systems with more polar diamine, for instance, with DDS for curing the rigid matrix. The electromicrograph of an epoxy thermoset, based on EPON 825, DDM, and 20% of vernonia oil, dodecanediamine B-staged material, shows vernonia rubbery particles with a broad distribution in the range of 5 to 30 microns diameter (Figure 3). The glass transition temperatures of the rubbery phase and the rigid epoxy matrix of this thermoset are observed in DMA at -22° and 160°C, respectively (Figure 4).

Our initial results show improved fracture toughness (K_{IC}), impact resistance and lower water absorption for so modified epoxy resins and coatings. The introduction of vernonia oil into commercial epoxy resins will also result in price reduction. Detailed description of our results is in preparation.

5. CONCLUSION

Vernonia oil, a naturally occuring epoxidized vegetable oil, has a unique structure with reactive epoxy rings, double bonds, lower viscosity than other industrially produced epoxidized vegetable oils, and a low melting point. It is an attractive reactive diluent for preparation of high solids alkyds and epoxy coating formulations.

6. ACKNOWLEDGMENT

We gratefully acknowledge financial support by the South Coast Air Quality Management District, U.S. Agency for International Development, Paint Research Associates, and Michigan State. We also thank Dr. John C. Graham, Coatings Research Institute and Dr. Robert Perdue, U.S. Department of Agriculture, for advice and many fruitful discussions. All DMA measurements have been carried out with a thermal analyser, kindly donated by TA Instruments (formerly DuPont Instruments).

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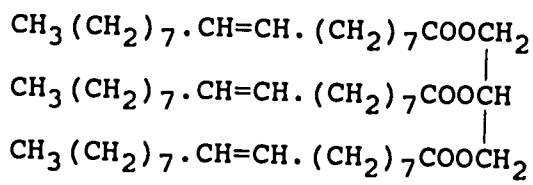
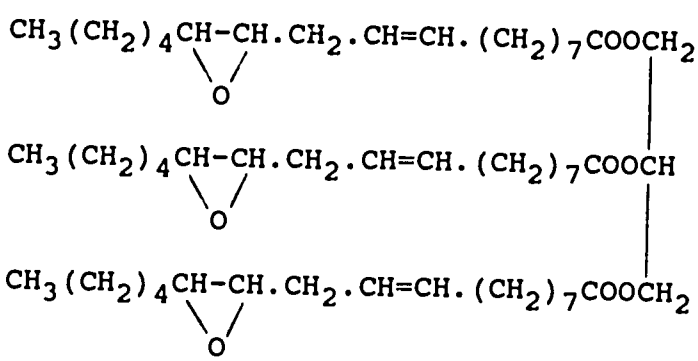
FIGURE 1. Molecular structure of triolein, vernonia oil, and epoxidized soybean oil

TRIOLEIN:



VERNONIA OIL:



EPOXIDIZED SOYBEAN OIL:

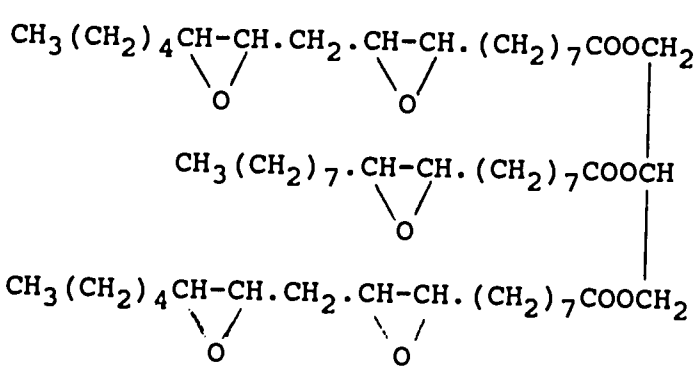


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FIGURE 2. Gel permeation chromatography of vernonia oil (a) and epoxidized soybean oil (b).

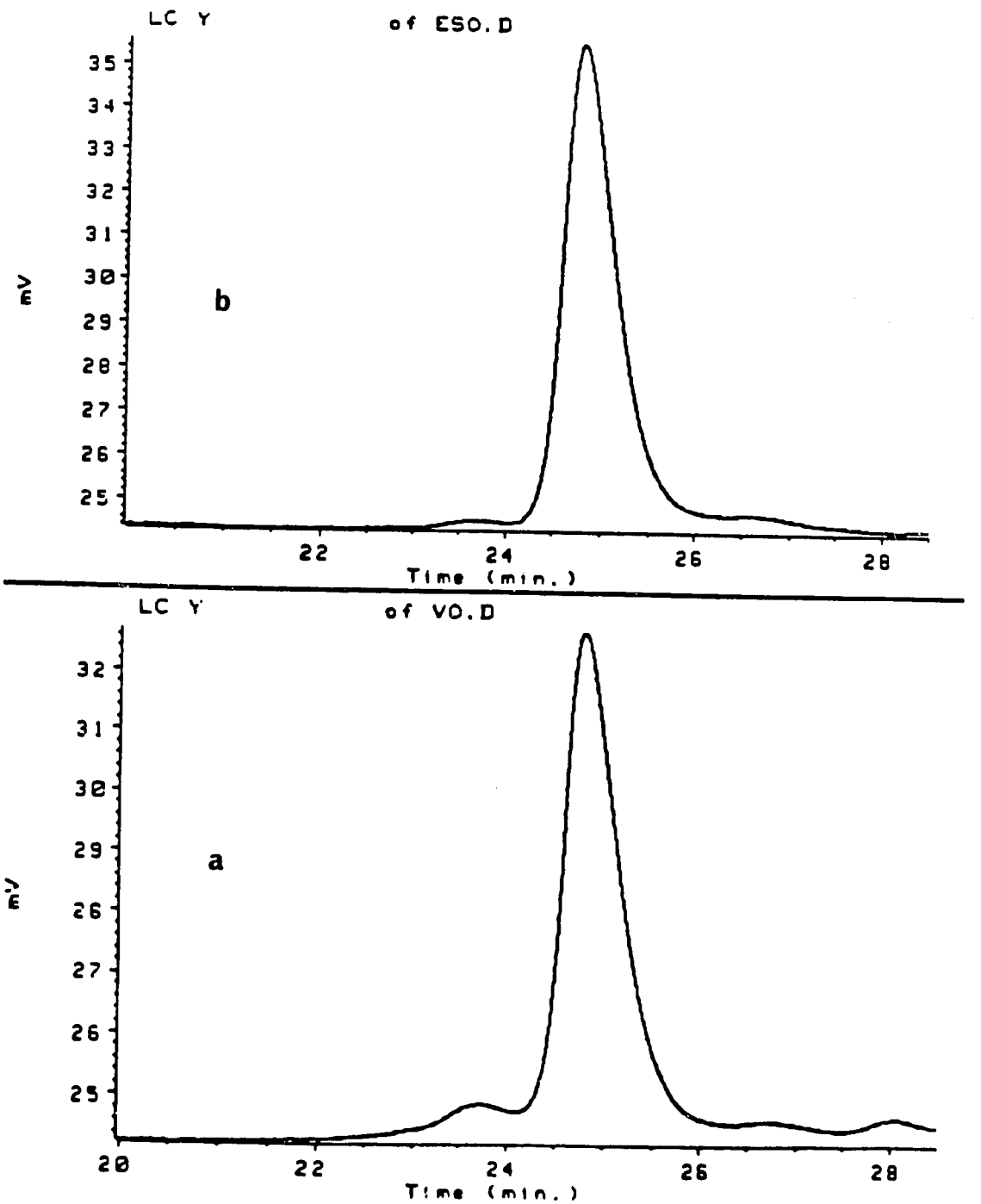

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FIGURE 3. Electromicrograph of a two-phase epoxy resin based on Epon 825, DDM, and 20% vernonia/dodecanediamine liquid rubber (B-staged material).

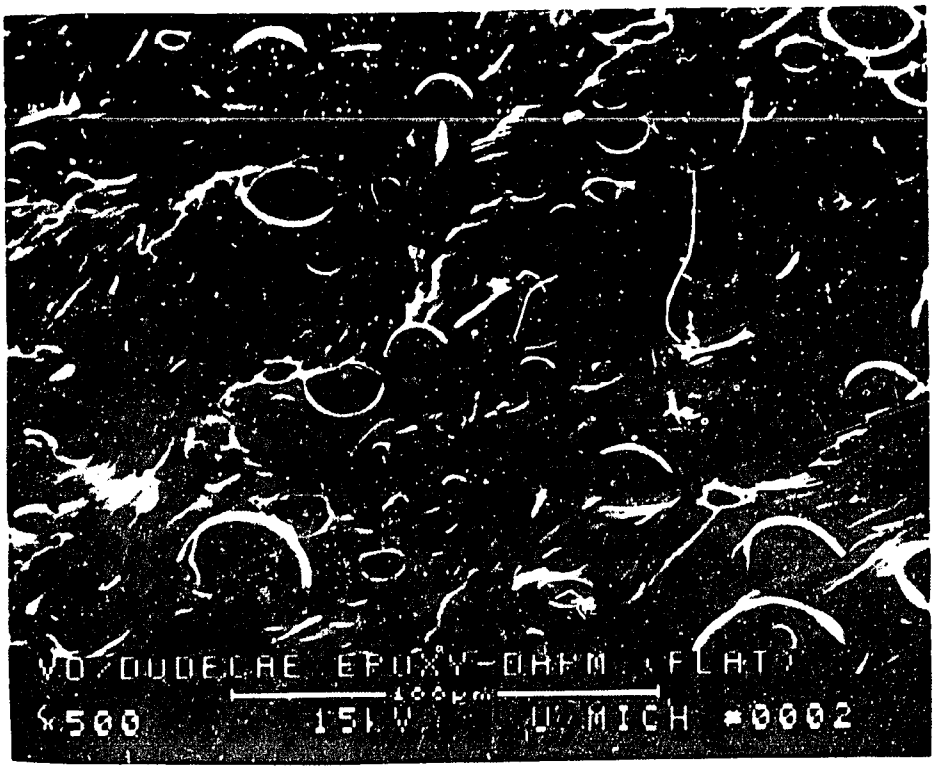

FIGURE 4. DMA of two-phase epoxy resin: matrix based on Epon 825 and DDM (Tg = 160°C) and rubbery particles (20%) of vernonia oil and dodecanediamine (Tg = -22°C).

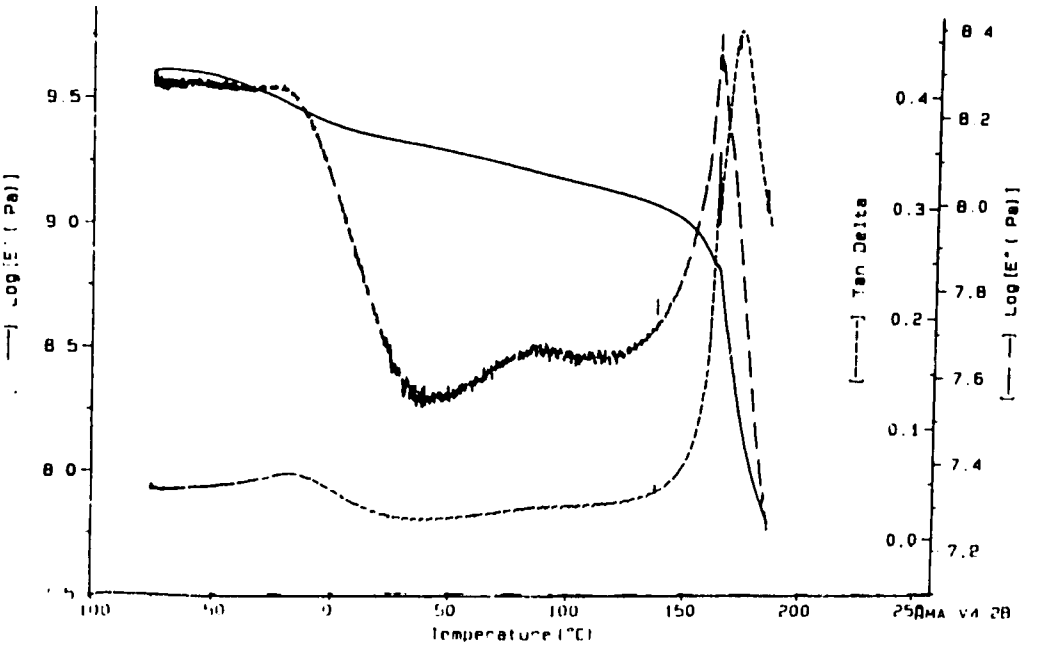

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TABLE 1. COMPOSITION OF PAINT FORMULATIONS BASED ON REICHHOLD BECKOSOL LONG OIL ALKYD 10-060 (WEIGHT PARTS)

10-060 LONG OIL ALKYD (70% SOLIDS)	78.60
ODORLESS MINERAL SPIRITS	23.59
BYK BYKUMEN	3.77
NUODEX NUXTRA CALCIUM 10%	1.12
PREMIX ABOVE	
DUPONT R-900 TiO2	150.97
T & W ATOMITE	37.74
NL CHEMICAL SD-1 BENTONE	2.72
ADD SLOWLY TO COWLS	
10-060 LONG OIL ALKYD	81.62
VERNONIA OIL	
ADD TO GRIND	
NUODEX NUXTRA COBALT 12%	0.46
NUODEX NUXTRA ZIRCO 24%	2.34
ODORLESS MINERAL SPIRITS	93.10
NUODEX EXKIN #2	1.62
PREMIX THEN ADD	

TABLE 2. DRIERS FOR VERNONIA OIL AND ITS MIXTURES WITH ALKYD RESINS

COBALT NAPHTHENATE
ZIRCONIUM DRIER
MANGANESE DRIER
CALCIUM DRIER

DRIER COMBINATIONS:
MOONEY DRIERS: Co, Ca, DRI-Rx
MOONEY DRIERS: Co, Mn, DRI-Rx
NUODEX NUXTRA COBALT
NUODEX NUXTRA ZIRCO
NUODEX NUXTRA CALCIUM
NUODEX ADR
BLENDED METALS/SURFACE DRIER
NUODEX LTD
COMPLEX OF METALS/THROUGH DRIER
NUODEX UTD
COMPLEX OF METALS/THROUGH DRIER
ACTIV 8
DRIER STABILIZER AND ACCELERATOR
MANCHEM MANOSEC CD-44
COBALT DRIER

TABLE 3. CHARACTERIZATION OF 2 MIL (52 MICRONS) THICK CLEAR COATINGS PREPARED UNDER BAKING CONDITIONS: COBALT DRIER 0.04%, 150°C, 1 HR., ON COLD ROLLED STEEL PANEL

	VERNONIA OIL	ALKYD (80%) VERNONIA OIL (20%)	ALKYD 10-560 10-060
ADHESION	4B	4B	4B
HARDNESS:			
PENCIL	H	2H	H
ROCKER	42	42	46
FLEXIBILITY	EXCELLENT	EXCELLENT	EXCELLENT
IMPACT STRENGTH:			
DIRECT, FT LB/IN[a]	150	150	160
REVERSE, FT LB/IN[a]	140	140	145

[a] 0.0534 FT LB/IN = 1 kJ/m

TABLE 4. CHARACTERIZATION OF PAINT FORMULATIONS

	PAINT FORMULATION	BROOKFIELD VISCOSITY CPS[a]	RCI DRYING TIME, HR	VOC LB./GAL.[b]
1.	INITIAL 10-060	2640	13	3.15
2.	VO 20%	586	11	3.11
3.	VO 20% LESS SOLVENT	2260	15	2.63
4.	VO 20% LESS SOLVENT	3476	12	2.52
5.	INITIAL 10-060 DRIER CD-44	3344	3-4	2.50
6.	DRIER CE-44 VO 20%	780	4	2.60

[a] 100 cps = 1 Pa.s
[b] 1 lb/gallon = 120 g/l

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18. S. Dirlikov (invited speaker), I. Frischinger, M.S. Islam, T. Lepkowski, P. Mutur', Vernonia Oil: A New Reactive Diluent for High Solids Alkyd and Epoxy Resins and Coatings, Engineering Society of Detroit and American Society of Manufacturers, Advanced Coatings Technology Conference, Dearborn, MI, June 1991, Conference Proceedings, 57-65.

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Akzo Coatings, Inc.

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VERNONIA OIL: A NEW REACTIVE DILUENT FOR HIGH SOLID ALKYD AND EPOXY RESINS AND COATINGS

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ABSTRACT

Vernonia oil has been evaluated for preparation of high solids coatings formulations by replacing conventional solvents. Vernonia oil is a natural epoxidized vegetable oil at a developmental stage in several countries. Trivernolin, the principal triglyceride, has a unique structure with three reactive epoxy groups and three carbon-carbon double bonds per molecule. Vernonia oil is characterized by very low viscosity, lower m.p., homogeneous molecular structure and potentially low price. It appears to be an attractive reactive diluent for low VOC alkyd and epoxy resins and coatings applications.

THE OBJECTIVE of our research is the application of vernonia oil as a reactive diluent for high solids alkyd, epoxy, and epoxy-ester coating formulations by replacing conventional solvents which produce VOC emissions.

There is an urgent need for reactive diluents for the reduction of conventional non-reactive solvents in coating formulations for air pollution control. Recently, further and stricter measures have been taken for reduction of air pollution. In 1988, the U.S. Environmental Protection Agency announced a ban on construction of major air-polluting plants in Los Angeles and other U.S. cities, and in the same year the South Coast Air Quality Management District announced a plan for reduction of hydrocarbon emissions in Orange County, California by 80 to 90% over the next five years. This plan requires reduction of volatile organic compound (VOC) emissions from paints and varnishes from the current 22.1 tons per day to 2.9 tons per day several years from now. It is an impossible task with today's coatings technology.

Vernonia oil, which is a naturally occurring epoxidized vegetable oil, contains predominantly trivernolin, a triglyceride of vernolic acid (Figure 1). Trivernolin contains three epoxy rings and three carbon-carbon double bonds per triglyceride molecule. There is one epoxy ring and one carbon-carbon double bond per each vernolic acid residue. Vernolic acid constitutes about 80% of the fatty acid residues of vernonia oil triglycerides.

VERNONIA GALAMENSIS

Vernonia galamensis, the source of vernonia oil, is a new potential oil seed crop for frost-free areas (Ref. 1-6). Some varieties grow in arid and semi-arid areas of the tropics and sub-tropics on land that is unsuitable for food crops. It is an annual weed. It has good seed retention and seeds germinate easily. It also has natural resistance to disease, nematodes, and most insects. Neither wild nor domestic animals consume Vernonia galamensis.

"Vernonia" seeds contain about 42% oil in contrast to soybeans, which contain only 17% oil. The maximum seed yield reached at this development stage is 2227 pounds per acre which compares favorably with an average yield of 1,926 pounds per acre for soybeans in the U.S. in 1979, the best

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yield for this crop in the U.S. from 1971 through 1984 (Ref. 2). Increased yields of vernonia seed are expected by breeding as greater genetic diversity becomes available.

In summary, it appears that the major agronomic problems for cultivation have been resolved. This new crop is currently at a developmental stage in several African countries, especially in Zimbabwe and Kenya and it has the potential to become a major industrial crop. Several major chemical and coatings companies have expressed strong interest in vernonia oil. Rhône-Poulenc (U.S.A. division) has started experimental crop trials for vernonia oil production, and several tons of Vernonia galamensis seeds are being harvested this year. Cargill is evaluating the possibilities for cultivation of Vernonia galamensis and the potential use of vernonia oil as well.

RESULTS AND DISCUSSION

PROPERTIES OF VERNONIA OIL. Vernonia oil has several unique features:

a. It is a transparent homogeneous liquid at room temperatue with excellent solubility in many organic solvents, diluents, and paints.
b. Vernonia oil has a low viscosity of 300 cps at 50°F and 100 cps at 85°F.
c. It has a low melting point of -36°F.
d. Vernonia oil has a homogeneous molecular structure consisting predominantly of identical triglyceride molecules which have three equal vernolic acid residues. In contrast, all other vegetable oils consist of a heterogeneous mixture of triglycerides with different fatty acid residues.
e. It is expected to be available at a low price in the range of $1.00-1.50 per pound.
f. Toxicity of vernonia oil is expected to correspond to that of the epoxidized soybean and linseed oils which are industrially produced.

VERNONIA VS. OTHER EPOXIDIZED VEGETABLE OILS. We believe that vernonia oil does not compete with other epoxidized vegetable oils, i.e. epoxidized soybean oil and epoxidized linseed oil, which are industrially produced by epoxidation of unsaturated vegetable oils and have structures similar to vernonia oil. Epoxidized soybean and linseed oils are less suitable for coatings applications as reactive diluents because of their higher viscosity.

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Both triolein and vernonia oil

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Results also show that vernonia oil dries at lower temperature and much faster than triolein. Good coatings have been obtained from vernonia oil at 150°C for half an hour. Triolein does not form coatings at 150°C for 1 hour. It forms coatings only at 180°C for 1.5 hours. The epoxy rings of vernonia oil probably activate the oxidation of the methylene group between the epoxy ring and the carbon-carbon double bond and therefore dries faster than triolein.

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All coatings have good adhesion of 4B. Hardness is also good. Pencil hardness is H and Rocker Sward hardness is 42. Both adhesion and hardness improve with higher baking temperature and longer time. Flexibility, according to a standard test by bending the steel panel around 180°, is excellent. We did not observe any cracks or tape-off under the microscope. The impact strength is also excellent. The direct impact strength is 150 pounds.inch; the reverse is 140 pounds.inch.

All three types of coatings have the same properties which indicates that introduction of vernonia oil does not deteriorate the basic properties of alkyd resins.

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The first paint formulation corresponds to the initial formulation based only on alkyd resin (Table 1).

In the second formulation, 20% of the alkyd has been substituted with vernonia oil. Lower viscosity is observed.

The next two formulations still contain 20% vernonia oil but their solvent content has been gradually reduced. The goal is to decrease the solvent to the point at which the viscosity of the paint formulation corresponds to the viscosity of the initial paint formulation without vernonia oil. These two formulations have much lower volatiles.

The fifth formulation is exactly as the first with the only difference being that it contains "our" new, more active CD-44 drier. Drying time of the paint formulations or tack-free

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time changes very little in the presence of vernonia oil, but sharply decreases in the presence of CD-44.

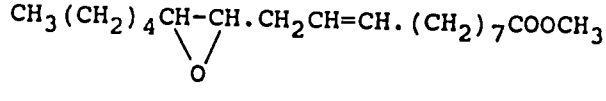
The last formulation contains the new drier system and 20% of its alkyd resin has been substituted with vernonia oil. The important result here is that by introducing 20% vernonia oil we are able to decrease the volatiles, and thus eventually reduce air-pollution, reduce the drying time, and maintain equal or lower viscosity than the initial paint formulation.

A potential problem for direct application of vernonia oil in alkyd formulations is an anticipated reaction between its epoxy groups and the terminal carboxyl groups of the alkyd resins. Our results show that vernonia oil does not change the can stability of the formulations. Obviously, the epoxy groups of vernonia oil have low reactivity and do not react with the free carboxyl groups of the alkyd resins under test conditions for can stability. The low reactivity of the vernonia oil epoxy groups was confirmed by additional experiments.

Q-UV test, which is a decrease in gloss at 20° and 60° after exposure to UV light and humidity for a week, indicates that vernonia oil improves the coatings weatherability.

MEDIUM OIL ALKYD PAINT FORMULATIONS. The effect of vernonia oil on paint formulations and coatings based on Reichhold Aroplaz 6440 medium oil alkyd resin is similar to that described above for long oil alkyds.

EPOXY REACTIVE DILUENTS. Vernonia oil contains reactive epoxy groups and our initial results show that it is an attractive reactive diluent for epoxy or epoxy ester formulations as well. Another possibility, again for epoxy formulations, is transesterification of vernonia oil with methanol or other higher molecular weight mono-functional alcohols for preparation of very low viscosity diluents. For example, methyl vernolate shown here has been prepared in quantitative yield:



Similar esters are industrially produced and the U.S. Navy has used them for coatings applications under water. They are very expensive.

MODIFICATION OF EPOXY RESINS AND COATINGS. The second part of the project is on application of vernonia oil for modification of commercially available epoxy resins and coatings. The project objective is simultaneous improvement of the two main disadvantages of epoxy resins: low toughness and high water absorption.

It is known that a small amount of discrete rubbery particles with an average size of several microns, randomly distributed in a glassy, brittle epoxy resin, dissipates part of the impact energy thus improving crack and impact resistance without deterioration of other properties of the initial epoxy resins.

Epoxy resin toughness is usually achieved by separation of a rubbery phase with a unimodal size distribution from the matrix during the curing process. Different carboxy- or amino-terminated (butadiene, siloxane, etc.) oligomers are used for the formation of the rubbery phase. Some of these oligomers are quite expensive. Vernonia oil, however, opens new opportunities. The epoxy resins based on vernonia oil and commercial amines are elastomers at room temperature. They have low glass transition temperatures, in the range of -80°C to 0°C, which depend on the nature of the diamine used for curing vernonia oil. They appear to be very suitable for toughening of commercial epoxies.

We obtained a two-phase epoxy thermosets and coatings with rubbery vernonia particles by using vernonia liquid rubbers (B-staged materials) as described in the experimental section. For this purpose, vernonia oil was initially B-staged with DDM or 1,12-dodecanediamine. Then homogeneous mixtures of commercial epoxy resin (EPON 825) and commercial amines (DDS, DDM, isophorone diamine, different aliphatic di- and polyamines, etc.), containing 10 to 25 percent vernonia oil B-staged material were cured according to a "standard" curing procedure for epoxy resin. The commercial epoxy resins have higher

reactivity with commercial diamines than the epoxy groups of vernonia oil. As a result, they form a rigid matrix at 70°C in which vernonia liquid droplets phase separate. The final thermoset is cured at 150°C. It consists of a rigid epoxy matrix with randomly distributed small rubbery "vernonia" spherical particles (Figure 3). Diamine molecules on the interface are expected to react with both the epoxy groups of the commercial epoxy resin and the unreacted epoxy groups of vernonia oil, and will presumably form a chemical bonding between the rigid matrix and the rubbery particles.

Several factors control phase separation. Miscibility of the initial mixture of epoxy resin, amine, and vernonia oil or its B-staged material, is required. Incompatibility and phase separation should start during the curing process before gelation for spherical morphology formation. Simultaneously, viscosity at this stage should be high to prevent coalescence and microscopic phase separation. The effective rubbery phase depends on the volume fraction of vernonia oil, nature of curing amine, and time and temperature regime of cure.

The particle diameter is a function of the incompatibility of vernonia B-staged material and the epoxy matrix. We have been able to vary the particle diameter in the range of the desirable particle size for toughening thermosets, e.g. from 0.3 to 50 microns. In general, larger particles are obtained for less compatible systems with more polar diamine, for instance, with DDS for curing the rigid matrix. The electromicrograph of an epoxy thermoset, based on EPON 825, DDM, and 20% of vernonia oil, dodecanediamine B-staged material, shows vernonia rubbery particles with a broad distribution in the range of 5 to 30 microns diameter (Figure 3). The glass transition temperatures of the rubbery phase and the rigid epoxy matrix of this thermoset are observed in DMA at -22° and 160°C, respectively (Figure 4).

Our initial results show improved fracture toughness (K_{IC}), impact resistance and lower water absorption for so modified epoxy resins and coatings. The introduction of vernonia oil into commercial epoxy resins will also result in price reduction. Detailed description of our results is in preparation.

EXPERIMENTAL

Vernonia oil has been kindly supplied by Dr. K. Carlson, U.S. Department of Agriculture. Its extraction from Vernonia galamensis seeds, refining and characterization is described in Ref. 7. The preparation of alkyd coatings formulations is shown in Table 1. The characterization of these formulations and their final coatings has been carried out according to the corresponding ASTMs.

Two-phase epoxy thermosets and coatings were prepared from vernonia oil which was initially B-staged with amines. A mixture of 100 g of vernonia oil and 25.63 g of 4,4'-methylenedianiline (DDM) was heated at 180°C for 40 hours under nitrogen. Similar results were observed for vernonia B-staged material obtained from 25.9 g of 1,12-dodecanediamine and 100 g of vernonia oil under the same conditions. The vernonia B-staged material based on DDM or 1,12-dodecanediamine was added in 10, 20 or 30 weight percent to a stoichiometric mixture of diglycidyl ether of bisphenol A (Shell epoxy resin EPON 825) and DDM or 4-aminophenyl sulfone (DDS). The resulting DDM homogeneous formulation is additionally B-staged at 75°C for 95 minutes under nitrogen, and then poured into the casting mold and vacuumed. Final cure and post-cure are carried out at 75°C for 4 hours and 150°C for two hours, respectively. The corresponding DDS formulation is B-staged at 150°C for 1 hour under nitrogen and then cured in the mold at 150°C for 2 hours. Both DDM or DDS formulations produce excellent large castings. Electromicrographs were taken by an Amray electron microscope, model 1000B.

CONCLUSION

Vernonia oil, a naturally occuring epoxidized vegetable oil, has a unique structure with reactive epoxy rings, double bonds, lower viscosity than other industrially produced epoxidized

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vegetable oils, and a low melting point. It is an attractive reactive diluent for preparation of high solids alkyds and epoxy coating formulations.

ACKNOWLEDGMENT

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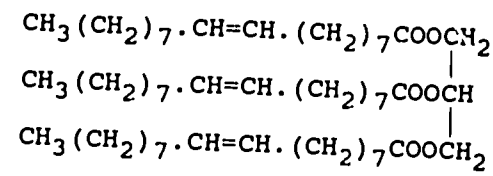
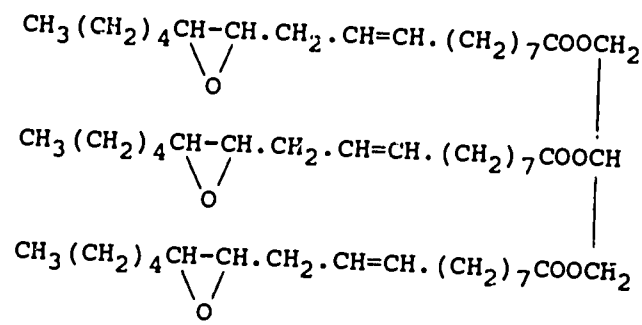
APPENDIX

FIGURE 1. MOLECULAR STRUCTURE OF TRIOLEIN, VERNONIA OIL, AND EPOXIDIZED SOYBEAN OIL

TRIOLEIN:



VERNONIA OIL:



EPOXIDIZED SOYBEAN OIL:

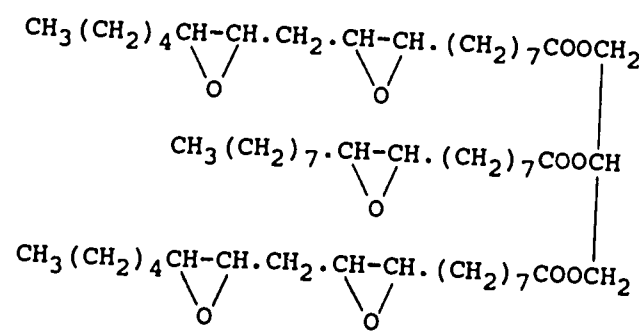


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FIGURE 2. GEL PERMEATION CHROMATOGRAPHY OF VERNONIA OIL (a) AND EPOXIDIZED SOYBEAN OIL (b).

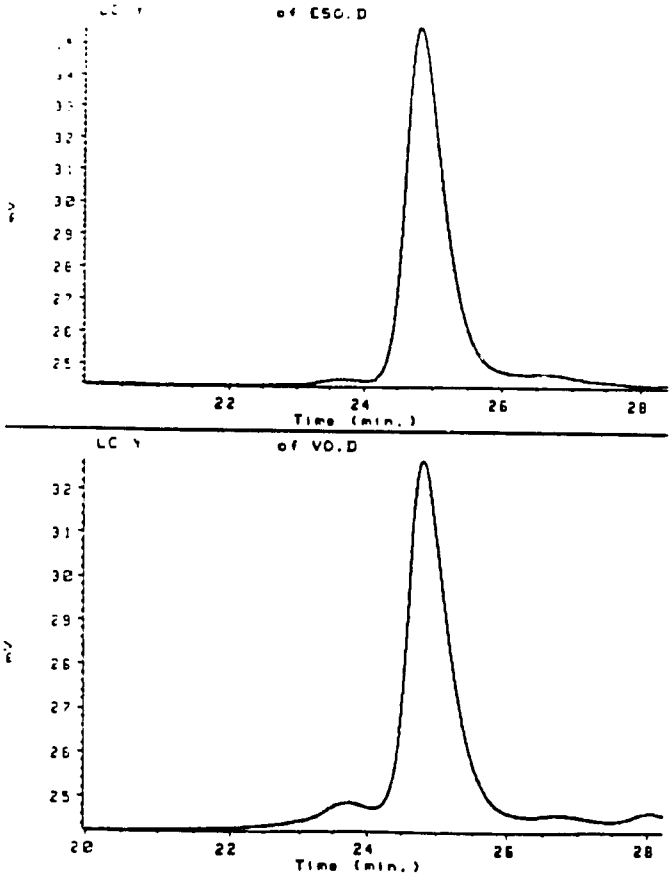

FIGURE 3. ELECTROMICROGRAPH OF A TWO-PHASE EPOXY RESIN BASED ON EPON 825, DDM, AND 20% VERNONIA/DODECANEDIAMINE LIQUID RUBBER (B-STAGED MATERIAL).

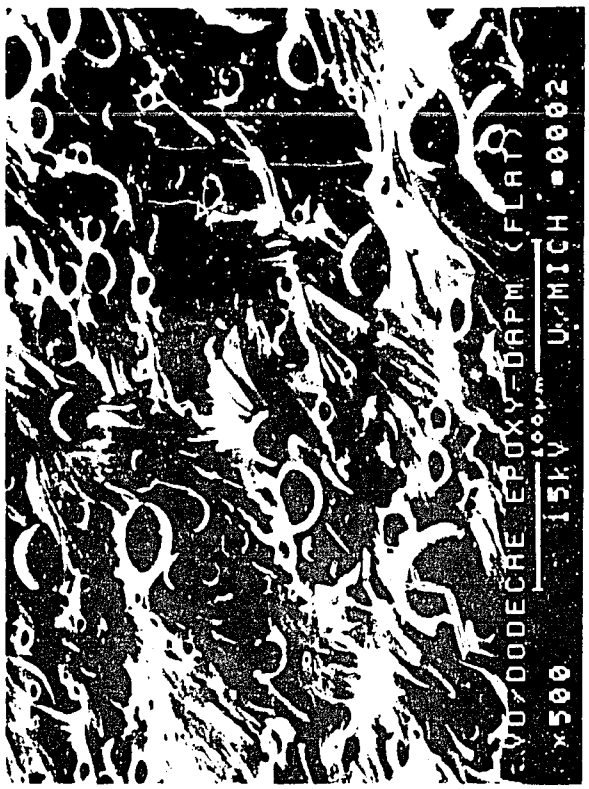

FIGURE 4. DMA OF TWO-PHASE EPOXY RESIN: MATRIX BASED ON EPON 825 AND DDM (Tg = 160°C) AND RUBBERY PARTICLES (20%) OF VERNONIA OIL AND DODECANEDIAMINE (Tg = -22°C)

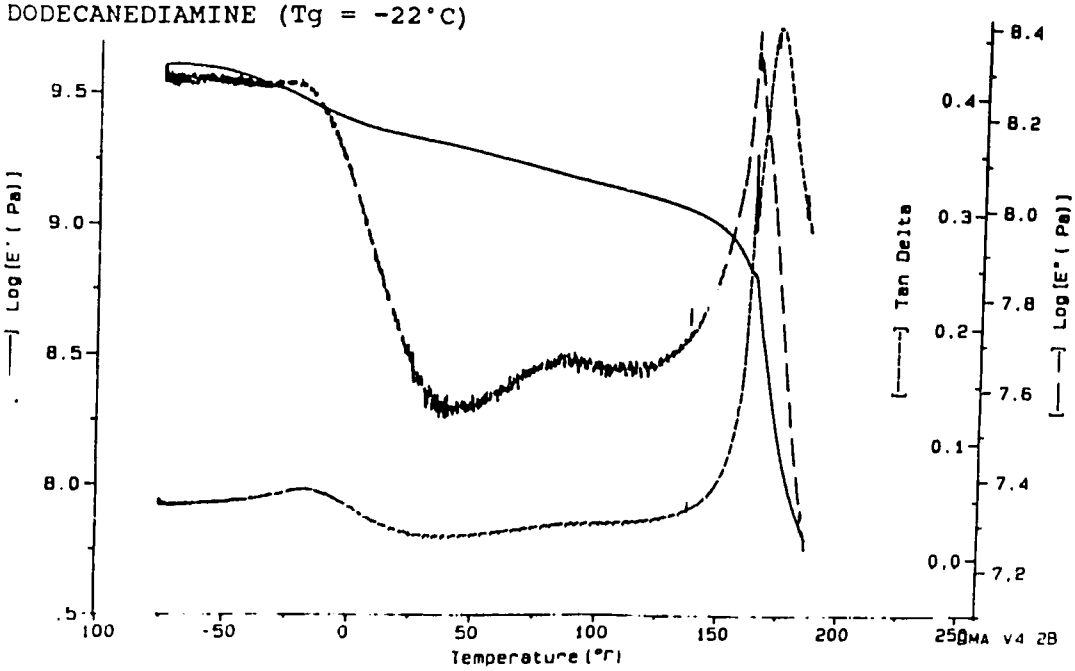

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TABLE 1. COMPOSITION OF PAINT FORMULATIONS BASED ON REICHHOLD BECKOSOL LONG OIL ALKYD 10-060 (WEIGHT PARTS)

10-060 LONG OIL ALKYD (70% SOLIDS)	78.60
ODORLESS MINERAL SPIRITS	23.59
BYK BYKUMEN	3.77
NUODEX NUXTRA CALCIUM 10%	1.12
PREMIX ABOVE	
DUPONT R-900 TiO2	150.97
T & W ATOMITE	37.74
NL CHEMICAL SD-1 BENTONE	2.72
ADD SLOWLY TO COWLS	
10-060 LONG OIL ALKYD	81.62
VERNONIA OIL	
ADD TO GRIND	
NUODEX NUXTRA COBALT 12%	0.46
NUODEX NUXTRA ZIRCO 24%	2.34
ODORLESS MINERAL SPIRITS	93.10
NUODEX EXKIN #2	1.62
PREMIX THEN ADD	

TABLE 2. DRIERS FOR VERNONIA OIL AND ITS MIXTURES WITH ALKYD RESINS

COBALT NAPHTHENATE
ZIRCONIUM DRIER
MANGANESE DRIER
CALCIUM DRIER

DRIER COMBINATIONS:
MOONEY DRIERS: Co, Ca, DRI-Rx
MOONEY DRIERS: Co, Mn, DRI-Rx
NUODEX NUXTRA COBALT
NUODEX NUXTRA ZIRCO
NUODEX NUXTRA CALCIUM
NUODEX ADR
BLENDED METALS/SURFACE DRIER
NUODEX LTD
COMPLEX OF METALS/THROUGH DRIER
NUODEX UTD
COMPLEX OF METALS/THROUGH DRIER
ACTIV 8
DRIER STABILIZER AND ACCELERATOR
MANCHEM MANOSEC CD-44
COBALT DRIER

TABLE 3. CHARACTERIZATION OF 2 MIL THICK CLEAR COATINGS PREPARED UNDER BAKING CONDITIONS: COBALT DRIER 0.04%, 150°C, 1 HR., ON COLD ROLLED STEEL PANEL

	VERNONIA OIL	ALKYD (80%) VERNONIA OIL (20%)	ALKYD 10-560 10-060
ADHESION	4B	4B	4B
HARDNESS:			
PENCIL	H	2H	H
ROCKER	42	42	46
FLEXIBILITY	EXCELLENT	EXCELLENT	EXCELLENT
IMPACT STRENGTH:			
DIRECT, LB.IN.	150	150	160
REVERSE, LB.IN.	140	140	145

TABLE 4. CHARACTERIZATION OF PAINT FORMULATIONS

	PAINT FORMULATION	BROOKFIELD VISCOSITY CPS	RCI DRYING TIME, HR	VOC(1) LB./GAL.
1.	INITIAL 10-060	2640	13	3.15
2.	VO 20%	586	11	3.11
3.	VO 20% LESS SOLVENT	2260	15	2.63
4.	VO 20% LESS SOLVENT	3476	12	2.52
5.	INITIAL 10-060 DRIER CD-44	3344	3-4	2.50
6.	DRIER CE-44 VO 20%	780	4	2.60

(1) 1 lb./gal. = 120 g/l

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