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Changes in Surfactants during Milling and Storage of Insecticide Water-Dispersible Powders

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A method for isolation and determination of anionic surfactants in insecticide water-dispersible powders has been developed and used to study changes in the surfactant during milling and storage. Sodium *N*-methyl-*N*-oleoyl taurate content of DDT powders was not affected by hammer milling but losses were

observed when the powder was air-milled. There were no surfactant losses when DDT powder was heated at 70° C. for 2 hours; gradual decomposition was observed when the powder was stored at 55° C. for 3 to 9 weeks or at ambient temperatures for 3 months or longer.

Water-dispersible powder formulations of insecticides are used widely in agriculture and public health applications. These powders usually are prepared by hammer- or air-milling the insecticide with an inert carrier, an anionic surfactant, and a dispersing agent. In the case of chlorinated hydrocarbon insecticides, changes in suspensibility of the formulations in storage usually can be traced to a growth of particle size or decomposition of the surfactant. The present investigation was conducted to study changes which take place in anionic surfactants during milling and storage of DDT powders. To measure the anionic surfactant, a method of isolation and determination had to be developed.

The reaction between anionic surfactants and methylene blue to form nonpolar adducts was used first by Jones (1945) as the basis for the colorimetric determination of the surfactant. In this method, the sample containing the anionic surfactant is diluted with water in a separatory funnel and excess methylene blue solution is added. Then the mixture is shaken with chloroform to extract the surfactant-methylene blue adduct. The absorbance of the blue chloroform layer is measured to determine the concentration of surfactant. Epton (1948) proposed a titrimetric method in which methylene blue is used as an indicator. A small amount of methylene blue is added to an aqueous solution of the anionic surfactant to be determined, then chloroform is added, and the surfactant-methylene blue adduct is extracted into the chloroform layer. The supernatant aqueous solution is titrated with a quaternary salt, cetyl pyridinium bromide. At the end point, the ionic form of the methylene blue is released, and the aqueous layer becomes blue. Veldhuis (1960) proposed the use of alkaline salts of polyhalogenated benzenesulfonic acids as primary standards for standardization of

the quaternary salt solution. He found the most satisfactory primary standard to be potassium trichlorobenzene sulfonate and used it to standardize the quaternary salt solution, Hyamine 1622, which was used to titrate the anionic surfactant.

Although Epton's method is accurate and convenient for determination of small amounts of anionic surfactants, it cannot be used for determination of the surfactant content of pesticide water-dispersible powders without first separating the surfactant from interfering materials. In particular, dispersing agents such as sulfonated lignins interfere in the determination of anionic surfactants by forming emulsions at the interface.

By careful selection of the solvent, anionic surfactants can be quantitatively extracted from pesticide water-dispersible powders without extracting the dispersing agents, then titrated with a quaternary salt solution using methylene blue as an indicator, by a procedure similar to that described by Epton.

In the proposed method, a 2-propanol-water (5 to 1) solution is used to extract the surfactant from the water-dispersible powder, and an aliquot of the extract is titrated with a standard solution of Hyamine 1622. Methylene blue is used as an indicator, and the end point is detected by migration of the blue color from the chloroform layer to the aqueous layer.

METHOD

Reagents. HYAMINE SOLUTION, 0.004*N*. Weigh approximately 1.82 grams of Hyamine 1622 (benzylidimethyl {2 - [2 - (*p* - 1,1,3,3 - tetramethylbutylphenoxy)ethoxy]-ethyl} ammonium chloride, monohydrate, Rohm and Haas Co., Washington Square, Philadelphia 5, Pa.) into a 1-liter volumetric flask and make to volume with water.

POTASSIUM 2,4,5-TRICHLOROBENZENE SULFONATE, STANDARD SOLUTION. Weigh accurately approximately 1.0 gram of potassium trichlorobenzene sulfonate (Baker and Adamson Division, Allied Chemical Corp., Morristown, N. J.) into a 1-liter volumetric flask and make to volume

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with water. Calculate the normality assuming the equivalent weight to be 299.6.

METHYLENE BLUE INDICATOR SOLUTION. Dissolve 0.03 gram of methylene blue, USP, and 50 grams of Na_2SO_4 in 500 ml. of water. Add 6.5 ml. of concentrated H_2SO_4 and dilute to 1 liter with water.

Procedure. STANDARDIZATION OF HYAMINE 1622 SOLUTION. Pipet 10 ml. of potassium 2,4,5-trichlorobenzene sulfonate standard solution into a 125-ml. F flask. Add 15 ml. of chloroform and 25 ml. of methylene blue indicator solution. Shake vigorously and allow the two layers to separate. Titrate with Hyamine 1622 solution, adding the titrant in small increments from a 25-ml. buret and shaking vigorously after each addition. As the end point is neared, a slight blue color will be observed in the aqueous layer and further additions should be made dropwise. At the end point the intensity of color in the chloroform and aqueous layers will be equal. The end point is best detected by tilting the flask, placing a finger over the interface, and observing the colored layers in strong transmitted light. From the volume of Hyamine 1622 required for the titration and the normality of the potassium trichlorobenzene sulfonate standard solution, calculate the normality of the Hyamine 1622 solution.

DETERMINATION OF ANIONIC SURFACTANT CONTENT OF A WATER-DISPERSIBLE POWDER. Weigh accurately into a 50-ml. F test tube an amount of the sample of water-dispersible powder containing 20 to 40 mg. of surfactant. Pipet 30 ml. of 2-propanol-water (5 to 1) solution into the tube and shake vigorously. Allow the tube to stand about 5 minutes and shake again. Allow the tube to stand until the supernatant liquid is clear at least to the mid-point of the tube. This may require an hour or more. Filter the clear solution through a Whatman No. 1 filter paper into a dry test tube and collect at least 15 ml. of filtrate. Pipet 15 ml. of the filtrate into a 125-ml. F Erlenmeyer flask and evaporate the solvent to near-dryness. Cool the flask, add 15 ml. of chloroform and 25 ml. of methylene blue indicator solution, and titrate with the standardized Hyamine 1622 solution as described above. Calculate the surfactant content as follows:

% anionic surfactant in sample =

$$\frac{2 \times \text{ml. (Hyamine)} \times \text{normality (Hyamine)} \times \text{mol. wt. of surfactant} \times 100}{\text{original weight of sample taken} \times 1000}$$

RESULTS AND DISCUSSION

The ratio of alcohol to water in the 2-propanol solution used to extract the surfactant from the water-dispersible powders is critical. If a higher concentration of water is used, some of the sulfonated lignin dispersants are extracted and interfere with the titration. If a higher concentration of alcohol is used, an excessive amount of the pesticide is extracted and this interferes.

Although small amounts of 2-propanol do not interfere with the titration, better results are obtained if most of the 2-propanol is evaporated prior to addition of the chloroform. The 125-ml. F Erlenmeyer flask is more satisfactory as a titration vessel than the cylinder used by Epton. The shaking time required for equilibration of the methylene blue between the chloroform and the aqueous

layers is less when the flask is used, and color matching is satisfactory. However, for highest accuracy, color matching is carried out better in a glass-stoppered mixing cylinder.

Although the reaction between the cationic surfactant used as the titrant and the anionic surfactant titrated appears to be stoichiometric, a considerable error is observed when very small samples are titrated. The consumption of titrant per milligram of three common anionic surfactants is shown in Figure 1. The deviation from linearity is believed to be due to the small amount of anionic surfactant which is bound with the methylene blue and remains in the chloroform layer when the titration is carried to the prescribed end point. This small loss becomes negligible when larger quantities of surfactant are titrated. High concentrations of anionic surfactant cause difficulty by producing emulsions at the interface as the end point is reached. To avoid these difficulties, the aliquot of the sample taken for analysis should fall within the following ranges: Conco AAS90G, 8 to 16 mg.; Igepon T-77, 8 to 20 mg.; and Conco WA dry, 10 to 30 mg. Ranges for other compounds should be determined experimentally.

Recovery of Surfactants from Powder Formulations. A series of DDT and dieldrin water-dispersible powders of known composition was prepared by grinding the carefully weighed ingredients in a mortar and pestle. The resulting homogeneous powders were sampled and analyzed by the procedure described above (Table I). Excellent recovery was obtained on all anionic surfactants tested both with and without added dispersant. In addition to the dispersant Marasperse-N, experiments were conducted with Polyfon-F and Polysect-100 with similar results. In the case of the dieldrin powders, a blank correction was necessary. When a 1-gram sample of dieldrin 75% water-dispersible powder without surfactant was analyzed according to the procedure described, 0.25 ml. of 0.004N Hyamine 1622 solution was required to reach the end point. All titrations of samples containing dieldrin were corrected for this blank.

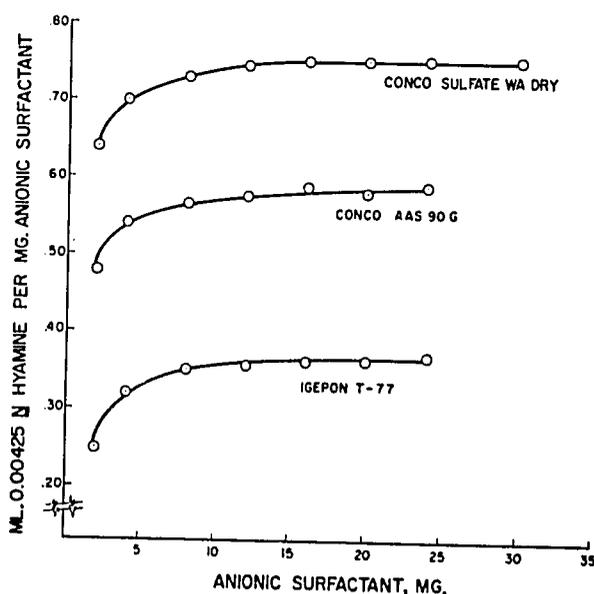


Figure 1. Effect of sample size on consumption of Hyamine solution by various anionic surfactants

Table I. Recovery of Anionic Surfactants from Water-Dispersible Powders

| Formula | Composition of Formulation, % | | | | | | | | | Anionic Surfactant Recovered | | |
|---------|-------------------------------|----------|--------|----------|-------------------------|---------------------|----------------------|-----------------------|------------------------|------------------------------|------|------------------|
| | DDT | Dieldrin | Hi-Sil | Attaclay | Marasperse ^a | Igepon ^b | Wetanol ^c | Tensaryl ^d | Conco AAS ^e | Duponol ^f | % | % of theoretical |
| 1 | 75.0 | | 19.0 | 2.0 | 2.0 | 2.00 | | | | | 2.00 | 100.0 |
| | | | | | | | | | | | 2.00 | 100.0 |
| 2 | 75.0 | | 19.0 | 2.0 | 2.0 | | 2.00 | | | | 2.03 | 101.5 |
| | | | | | | | | | | | 2.00 | 100.0 |
| 3 | 75.0 | | 19.0 | 2.0 | 2.0 | | | 2.00 | | | 2.00 | 100.0 |
| | | | | | | | | | | | 2.00 | 100.0 |
| 4 | 75.0 | | 19.0 | 4.0 | | 2.00 | | | | | 2.00 | 100.0 |
| | | | | | | | | | | | 1.99 | 99.5 |
| 5 | | 75.0 | 19.0 | 2.0 | 2.0 | 2.00 | | | | | 1.99 | 99.5 |
| | | | | | | | | | | | 1.96 | 98.0 |
| 6 | | 75.0 | 19.0 | 2.0 | 2.0 | | | 2.00 | | | 2.01 | 100.5 |
| | | | | | | | | | | | 2.02 | 101.0 |
| 7 | | 75.0 | 19.0 | 2.0 | 2.0 | | | | 2.00 | | 1.98 | 98.0 |
| | | | | | | | | | | | 2.04 | 102.0 |
| | | | | | | | | | | | 2.01 | 100.5 |
| 8 | | 75.0 | 19.0 | 4.0 | | 2.00 | | | | | 1.98 | 99.0 |
| | | | | | | | | | | | 1.97 | 98.5 |

^a Marasperse-N, sodium lignosulfonate (American Can Co., New York).
^b Igepon T-77, 67% *N*-methyl-*N*-oleoyl taurate (General Aniline and Film Corp., New York).
^c Wetanol, modified sodium salt of sulfated fatty alcohol (Glyco Chemicals, New York).
^d Tensaryl, sodium octyl benzene sulfonate (Tensia, Sacrete Anonyme, Liege, Belgium).
^e Conco AAS-90G, 90% sodium dodecyl benzene sulfonate (Continental Chemical Co., Clifton, N. J.).
^f Duponol WA-dry, sodium lauryl sulfate (E. I. du Pont de Nemours & Co., Wilmington, Del.).

Accuracy and Precision. The accuracy of the method is illustrated by the data in Table I. The precision was tested by repetitive analysis of a single thoroughly mixed sample of DDT powder containing Igepon T-77, which was analyzed 54 times over a period of one week. The average content observed was 1.52%, with all results falling in the range 1.46 to 1.57%. The standard deviation was calculated to be 0.025.

Losses of Surfactant Observed in Milling and Storage of Water-Dispersible Powders. A sample of commercially prepared 75% DDT powder containing Hi-Sil, Attaclay, Polyfon-F, and Igepon T-77 was passed through a laboratory hammer mill 50 consecutive times. After each second milling, a sample was taken and analyzed in duplicate for the anionic surfactant. No loss of surfactant was observed even after 50 passes through the hammer mill. On the other hand, a similar formulation, when passed through a laboratory air mill only seven times, lost approximately 10% of the initial surfactant (Table II). Even more serious losses were observed in powders which had passed through commercial air mills. Some 98 samples of DDT powder were collected from different manufacturers and analyzed for sodium *N*-methyl-*N*-oleoyl taurate. None of the samples yielded the quantity of surfactant initially charged in the formulation. The average loss in the milling operation was 15.6%.

A series of DDT, 75% water-dispersible powders was obtained from commercial production for studies on the effect of heat and long-term storage on surfactant content. Although the samples were taken from several manufacturers, the anionic surfactant in all cases was Igepon T-77. The temperatures selected were 70° C. for short-term tests and 55° C. for intermediate-term tests. The 70° C. treatment for 2 hours was of particular interest

because this treatment is required by the specifications of the Agency for International Development and the World Health Organization for DDT powders used in the World Malaria Eradication programs. The 70° C. treatment was carried out in large test tubes suspended in an oil bath exactly as described in the above specifications. The 55° C. storage was carried out in a forced draft oven with the samples contained in 250-ml. beakers equipped with loosely fitting disks designed to exert a pressure of 25 grams per sq. cm. on the surface of the powder. After the appropriate heat treatment, the samples were analyzed for anionic surfactant according to the method described.

The data from these tests (Table III) show that heating the samples for 2 hours at 70° C. has no effect on the surfactant content. However, significant losses were ob-

Table II. Changes in Surfactant Content during Air and Hammer Milling

| No. of Passes | Igepon T-77 Found, % | |
|---------------|----------------------|-------------|
| | Air mill | Hammer mill |
| 0 | 1.67 | 1.56 |
| 1 | 1.66 | |
| 2 | 1.60 | 1.55 |
| 3 | 1.60 | |
| 4 | 1.52 | 1.53 |
| 5 | 1.53 | |
| 6 | 1.51 | 1.53 |
| 7 | | |
| 10 | | 1.50 |
| 20 | | 1.51 |
| 30 | | 1.54 |
| 40 | | 1.50 |
| 50 | | 1.55 |

Table III. Changes in Surfactant Content of Water-Dispersible Powders during Accelerated Storage Treatment and Storage

| Sample No. | Surfactant ^a Content Found, % | | | | | | |
|------------|--|---------------------------------|------------------|------------|------------|-------------------------------|-------|
| | Initial | Heated 2 hr. at 70° C. | Stored at 55° C. | | | Stored at Ambient Temp. | |
| | | | 3 weeks | 6 weeks | 9 weeks | 3 mo. | 8 mo. |
| 173 | 1.37 | 1.37 | | | | 1.21 | |
| 187 | 1.63 | 1.61 | | | | 1.27 | |
| 197 | 1.38 | 1.38 | | | | 1.15 | |
| 202 | 1.36 | 1.33 | | | | 1.09 | |
| 1a | 1.28 | | 1.13 | 1.08 | 0.90 | 1.09 | |
| 3a | 1.33 | | 1.28 | 1.06 | 1.03 | 1.21 | |
| 16a | 1.17 | | 1.09 | 0.97 | 0.85 | 1.04 | |
| 18a | 1.15 | | 1.03 | 0.93 | 0.84 | 1.03 | |
| 21a | 1.18 | | 1.05 | 0.94 | 0.83 | 0.97 | |

^a All samples were from commercial production and surfactant used was Igepon T-77.

served in all cases where samples were held in storage at 55° C. for intermediate terms or at ambient temperatures for long terms. Although the data are not presented here, all DDT water-dispersible powder samples found to contain less than 1% surfactant exhibited lowered suspensibility values. Samples with less than about 0.9% surfactant flocculated when suspended in water.

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