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FACTORS AFFECTING THE SUSPENSIBILITY OF DDT WATER-DISPERSIBLE POWDERS *

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SYNOPSIS

The authors describe some experiments carried out to determine the effect of moisture, temperature, and pressure on the suspensibility of DDT water-dispersible powders.

It was found that the removal of moisture brought about a slight increase in suspensibility; that heating for one hour at temperatures below 70°C resulted in an increase in suspensibility, due probably to the drying effect of the heat, whereas heating for the same period at temperatures above 70°C resulted in a decrease; that on prolonged heating at 70°C and 75°C the suspensibility decreased sharply in the first four hours but thereafter showed little change up to 20 hours; and, finally, that low pressures—for example, 25 g per cm²—had little effect on the suspensibility, but that at pressures of 100 pounds per square inch (7 atm.) and over, it varied in inverse proportion to the logarithm of the pressure.

The most reliable criterion for evaluation of the quality of a water-dispersible insecticide powder designed to be used in hand spraying equipment has proved to be the suspensibility test. This test has been incorporated in the specifications for water-dispersible insecticide powders suitable for use in malaria control programmes drawn up by the International Cooperation Administration (ICA)[1] and by the World Health Organization.[2] Presumably all powders change to some extent when stored for long periods of time. This change is usually evidenced by a decrease in suspensibility. Loss of suspensibility during storage will vary with the formulation and sometimes even within the same formulation.

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[1] International Cooperation Administration (1955, 1956, 1958) *DDT, 75 percent, water-dispersible powder*, Washington, D.C. (ICA Specification No 101055, 10 October 1955; revised 10 August 1956 and issued as ICA Specification No. 81056; revised 4 September 1958 and issued as ICA Specification No. 9458)

[2] World Health Organization (1956) *Specifications for pesticides*, Geneva, p. 105

Two major factors which appear to affect changes in suspensibility during storage are increase in particle size (from agglomeration of individual particles) and deterioration of the surfactants or changes in their physical association with the particles. There are probably other factors involved which may affect suspensibility during storage, but if so they have not become evident in the authors' experience. Increase in particle size seems to be the main reason for the decrease in suspensibility during storage, but changes in the surfactants cannot be clearly eliminated as a contributing factor or even as the major factor involved in some cases. Pearce, Goette & Sedlak [1] have cited one instance where deterioration of the surfactants was the sole cause of poor suspensibility.

If the loss of suspensibility is due to deterioration of one of the surfactants, it may be indicated by the addition of fresh surfactant. If the suspensibility returns to a reasonable value it can be assumed that the failure was due primarily to deterioration of one of the surfactants. The rapid settling of the particles in this case results from agglomeration of the individual particles into aggregates, but since addition of surfactant will restore the suspensibility of the material it indicates that the individual particles have not lost their identity. This type of agglomeration, a loose aggregate consisting of discrete particles which can be dispersed by the addition of a surfactant or by mild agitation, is defined as reversible agglomeration for the purpose of this presentation.

On the other hand, if the particles in a given sample undergo fusion, an agglomerate is formed which can be subdivided only by remilling. Neither addition of surfactant nor agitation will markedly increase the suspensibility of a powder which has undergone a substantial change of this nature. This phenomenon is defined as irreversible agglomeration. Most, if not all, powders will undergo such a change upon long-term storage, especially at elevated temperatures. All powders can be made to agglomerate in this manner by application of heat or pressure.

Another type of agglomeration, caking, is sometimes encountered in water-dispersible powders. Caking is a gross form of agglomeration and may be reversible, irreversible or a mixture of the two, depending upon the physical association of the particles. If fully reversible, powders exhibiting severe caking can be satisfactorily suspended if the material is thoroughly wetted by pasting or soaking.

Some water-dispersible powders exhibiting high initial suspensibilities deteriorate upon long-term storage, especially if they are subjected to high temperatures. A laboratory test which would indicate the probable storage stability under tropical storage conditions would be desirable. The so-called " tropical storage pre-treatment " recommended in the current ICA and WHO specifications has not proved adequate for this purpose. Pearce

[1] See article on page 921.

et al.[1] have presented data which provide evidence that storage of water-dispersible powders at relatively high temperatures over appreciable periods of time would indicate their probable storage stabilities over longer periods of time under ordinary storage conditions. Even though valuable information was gained from this work, the relatively long periods of time required would limit the use of this method as a practical laboratory test. A similar test which would yield the same information in a short period of time is needed. A programme of study has been undertaken to investigate the factors affecting suspensibility with the object of developing such a laboratory test, and the initial results of this investigation are described below.

Effect of Drying on Suspensibility

In specifications for DDT water-dispersible powders requiring a suspensibility test, the determination is made on the sample " as received ". This is practical, since the suspensibility test is designed to simulate actual suspensibility in the field and the powders are used without further treatment. We have been advised by other investigators that moisture content influences suspensibility. Earlier studies carried out in our laboratory to determine the influence of moisture gave inconclusive results. In connexion with the studies on the effects of high-temperature treatment on suspensibility, it became necessary to evaluate the effect of drying on suspensibility, since this occurs during any extended heat treatment of a powder. Accordingly, the following experiment was conducted.

Several samples of 75% DDT powder were weighed and placed in a vacuum desiccator over drierite. The samples were maintained under a vacuum of approximately 100 mm Hg and weighed at 24-hour intervals. All samples came to constant weight within 24 hours. Suspensibilities were determined on the samples " as received " [2] and after drying. All determinations were made on the basis of the undried samples according to ICA Specification No. 9458 for 75% DDT water-dispersible powders. The data are given in Table 1. The " as received " suspensibility values are averages of duplicate runs. Other values include both single and replicate runs. A small, but consistent, increase in suspensibility was observed on removing moisture from the samples.

Effect of Temperature on Suspensibility

As indicated above, one of the objects of this study was to develop a rapid laboratory procedure which would replace the high-temperature long-term storage methods used by Pearce et al.[1] for evaluating storage

[1] See article on page 921.

[2] Throughout this paper reference to suspensibility values " as received " indicates values obtained at the beginning of the experiment, even though some samples were six months old or older.

TABLE 1. EFFECT OF DRYING ON SUSPENSIBILITY OF 75% DDT WATER-DISPERSIBLE POWDERS

Sample No.	Weight loss on drying (%)	Suspensibility		Percentage increase
		as received	dried	
86	1 7	1.61	1.68	4 3
42	1.3	0.96	1 00	4.2
94	1 9	1.61	1.71	6 2
07	1.8	1.62	1.78	9.9
2	1.6	1.61	1.68	4 3
7	—	0.96	1.00	4 2
10	—	1.61	1.71	6.2
13	—	1.62	1.78	9.9

stability. Since irreversible agglomeration of particles is apparently a rate phenomenon, we have studied the changes produced by subjecting the sample to various temperatures while holding the time constant, as well as those produced by varying the time while holding the sample at a given temperature. The experiment in which temperature was varied with time constant will be presented first.

A series of 23 samples of 75% DDT was tested for suspensibility as received and after heating for one hour at temperatures ranging from 60°C to 80°C. The heat treatment was carried out by placing 3.33 g of the powder in a 100-ml beaker and placing the beaker in an oven held at the desired temperature, controlled within ± 1°C. After removal from the oven, the open samples were cooled in air before the suspensibility determination was made. The data are presented in Table 2. It will be observed that in most cases the suspensibilities of samples held at 60°C for one hour exhibited an increase in suspensibility. Some samples retained high suspensibility values even after heating at 70°C.

The increases in suspensibility observed after heating for one hour at temperatures up to 70°C are of the same order of magnitude as those found in the drying experiment above, and it is believed that the increase in suspensibility can be best explained on this basis. This was further substantiated by measuring the loss of weight on drying at 60°C for one hour. These losses were very nearly the same as those observed upon drying in a vacuum desiccator over drierite for 24 hours.

In the second phase of the elevated temperature experiment, some of the same samples were heated at a given temperature for varying periods of time up to 20 hours. The change in suspensibility with time at the various temperatures tested is given in Table 3. The changes observed at 60°C and

TABLE 2. SUSPENSIBILITIES OF 75% DDT WATER-DISPERSIBLE POWDERS AS RECEIVED AND AFTER HEATING FOR ONE HOUR AT VARIOUS TEMPERATURES

Sample No.	As received	60°C	65°C	70°C	75°C	80°C
1	1.28	1.58	1.50	1.36	0.92	0.72
2	1.61	1.79	1.66	1.64	1.12	1.00
3	1.64	1.81	1.56	1.41	0.96	0 60
4	1.75	1.95	1 60	1.60	1 04	0.78
5	1.73	1 89	1.92	1.78	1.34	1.20
6	1.24	1.74	1.59	1.46	1.24	0.80
7	0 96	1.25	1 11	1 05	0.87	0.88
8	1 65	1.91	1.73	1.66	1.38	1.17
9	1 19	1.13	1.08	0.86	0.51	0 45
10	1.61	1.78	1.65	1.43	1.03	0.84
11	1.45	1 58	1.49	1 52	1.05	0.85
12	1 72	1.93	1.77	1.79	1 07	0 79
13	1 62	1 77	1.65	1 39	1.04	0 81
14	1 79	2.06	1 98	1.85	1 24	1.14
15	0.96	1.39	1.34	1.10	0.78	0 53
16	0.57	0 75	0.80	0 64	0.83	0 45
17	1 03	0 81	0 58	0 44	0 28	0.15
18	1.48	1.70	1 56	1.43	1 19	0.76
19	1.44	1 66	1.55	1 40	1.12	0 72
20	1 57	1.65	1.61	1.34	1.00	0.70
21	1.53	1.76	1.60	1.17	1 26	0.86
22	1.50	1 60	1.60	1 41	1.20	0 82
23	1 50	1.65	1.59	1.38	1.16	0 90

65°C are small even after 20 hours. At higher temperatures, however, the behaviour simulates that of samples held at lower temperatures for long periods of time. For example, according to Pearce et al.[1] samples held at 65°C usually exhibit a sharp drop in suspensibility in about one week, followed by a gradual decrease over a period of 6-12 months. At 70°C and 75°C a similar drop is observed within four hours, followed by a gradual decrease. This levelling off may be observed in all powders, but the suspensibilities represented by the flat portion of the curve vary considerably. We

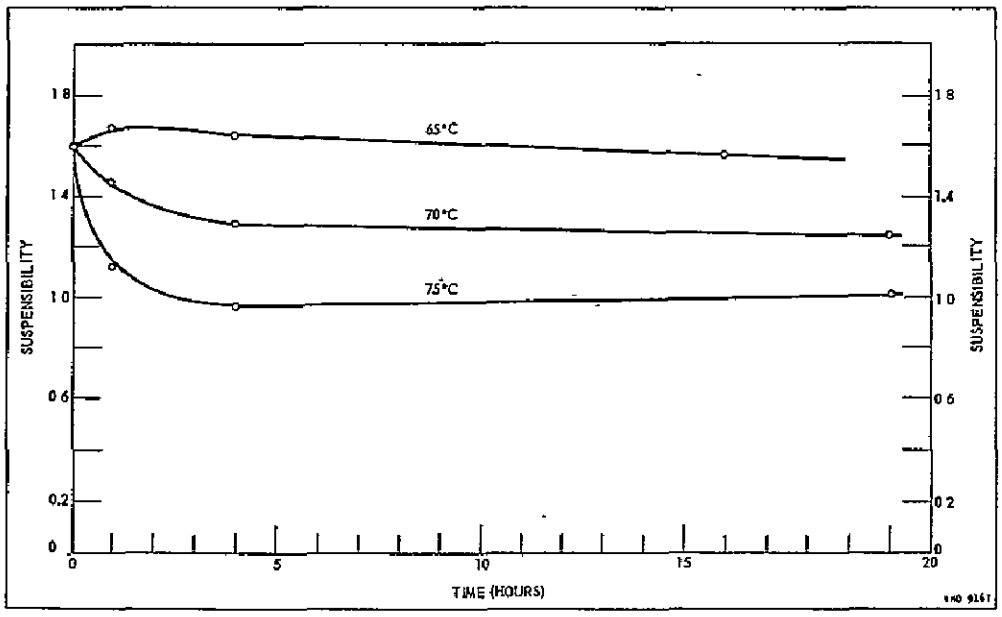
[1] See article on page 921.

TABLE 3. EFFECT OF TIME ON SUSPENSIBILITIES OF DDT WATER-DISPERSIBLE POWDERS HELD AT VARIOUS TEMPERATURES

Sample No.	Suspensibility as received	65°C			70°C			75°C		
		1 hour	4 hours	16 hours	1 hour	4 hours	20 hours	1 hour	4 hours	20 hours
3	1.64	1.56	1.50	1.34	1.41	1.07	1.00	0.96	0.77	0.80
7	0.96	1.11	1.22	1.16	1.05	1.01	1.01	0.89	0.96	0.83
8	1.65	1.73	1.67	1.60	1.66	1.34	1.34	1.38	1.21	1.17
13	1.62	1.65	1.64	1.50	1.39	1.29	1.12	1.04	0.98	0.93
16	0.57	0.80	0.62	0.50	0.64	0.54	0.45	0.83	0.41	0.44
20	1.57	1.61	1.49	1.40	1.34	1.14	1.04	1.00	0.91	0.83
24	1.60	1.72	1.75	1.62	1.51	1.46	1.46	1.21	1.11	1.10
25	1.60	1.74	1.82	1.76	1.42	1.39	1.32	1.10	0.82	1.14

believe that the suspensibilities in this plateau region are an indication of the relative stability of the powders tested. Further experiments are in progress to determine whether this assumption is valid. The average change in suspensibility with time at higher temperatures is presented graphically in Fig. 1. Samples 7 and 16 were omitted from the averages because they were old samples which had already reached their suspensibility plateau

FIG. 1. CHANGE IN AVERAGE SUSPENSIBILITY OF DDT WATER-DISPERSIBLE POWDERS WITH TIME*



* Based on data presented in Table 3

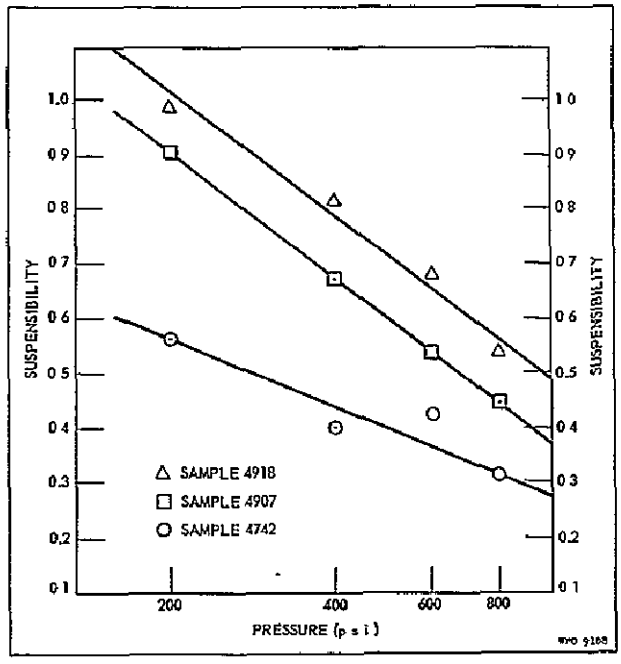
during storage. It is assumed that the slight initial rise in the curve representing samples held at 65°C is a result of the drying effect discussed above. The curves representing samples held at 70°C and 75°C are geometrically similar to those presented by Pearce et al.[1] from data obtained on powders held at 50°C and 65°C for periods of up to one year.

Effect of Pressure on Suspensibility

In an effort to discover some rapid test which would give an indication of the stability of a water-dispersible powder, it was decided to investigate the effects of high pressure on the powders. Somewhat drastic conditions (pressures of 100 pounds per square inch (p.s.i.)—i.e., 7 atm.—and above) were chosen in the hope that a good separation of stable and unstable powders could be made. Two experiments were carried out in this study. In one experiment the powders were subjected to various pressures for a given length of time, and in the other they were subjected to a given pressure for varying lengths of time.

A special mortar was constructed for compression of the samples. The mortar was similar to a commercial diamond mortar with a base and cylinder made of brass and a sleeve of stainless steel. The cylinder diameter was about one inch (2.5 cm) and the mortar depth 1½ inches (3.8 cm). The

FIG. 2. RELATION BETWEEN SUSPENSIBILITY OF DDT WATER-DISPERSIBLE POWDERS AND PRESSURE



[1] See article on page 921.

mortar was compressed in a Carver press fitted with a 0-1000 p.s.i. pressure gauge. Samples were held at pressures of 200, 400, 600, and 800 p.s.i. (14, 28, 42 and 56 atm.) for one minute each. A plot of suspensibility against log pressure is shown in Fig. 2. The resulting straight lines indicate the logarithmic relationship between pressure and suspensibility.

In a second experiment, several samples were subjected to a pressure of 100 p.s.i. for various lengths of time from 1 second to 20 minutes. The results tabulated in Table 4 indicate that at 100 p.s.i. the suspensibility is independent of the length of time the pressure is applied to the sample.

TABLE 4. SUSPENSIBILITY OF DDT WATER-DISPERSIBLE POWDERS SUBJECTED TO A PRESSURE OF 100 p.s.i.

Sample No	Suspensibility as received	Time						
		seconds		minutes				
		1	30	1	3	5	10	20
12	1.72	1.16	1 22		1 12		1.08	
25	1.60			1.26		1.28	1.33	1 27

A preliminary experiment, run on only three samples, indicated that the small amount of pressure applied to samples undergoing the tropical storage pre-treatment had no significant effect on the suspensibility. This pre-treatment procedure specifies that samples be held at 55°C for 20 hours under a weight exerting a pressure of 25 g per cm^2. The results of the experiment with DDT water-dispersible powders are in agreement with those obtained in a similar experiment conducted on dieldrin powders. At higher temperatures, however, the suspensibilities of samples weighted during the heat treatment were found to be consistently higher than the unweighted samples. This is true of both DDT and dieldrin powders. The data for the DDT powders are given in Table 5.

TABLE 5. COMPARISON OF SUSPENSIBILITIES OF 75% DDT WATER-DISPERSIBLE POWDERS AFTER HEATING WITH AND WITHOUT WEIGHTING

Sample No.	As received	55°C for 20 hours		80°C for 1 hour	
		No weight	25 g/cm²	No weight	25 g/cm²
1	1 34	1.57	1.50	0 68	1.00
2	1.11	0.82	0 80	0.13	0.24
3	1.56	1.66	1.75	0 71	0.91

RÉSUMÉ

Les effets de l'humidité et de la température sur l'aptitude des poudres mouillables à se mettre en suspension sont étudiés dans cet article. La poudre d'usage courant contient 1,5% d'humidité. La dessiccation par le vide ou la chaleur, à une température de 70°C au maximum améliore cette aptitude de 4-10%. Des températures supérieures ont un effet inverse.

Des échantillons de poudre dispersables dans l'eau ont été soumis à des températures de 65°, 70° et 75°C pendant des périodes allant jusqu'à 20 heures. La courbe indiquant l'aptitude à se mettre en suspension, illustrant les résultats d'essais effectués à 70°-75°C, tombe brusquement après 4 heures, puis s'élève à nouveau pour se maintenir sans changement appréciable jusqu'à 20 heures. Ce phénomène est caractéristique des poudres dispersables dans l'eau, et s'observe même à des températures plus basses maintenues pendant une plus longue période. Il semble, d'après ces essais préliminaires que le comportement des poudres dispersables, à 70° et 75°C, observé pendant un temps relativement court peut donner d'utiles indications sur leurs qualités de conservation. On poursuit actuellement l'étude du rapport entre le comportement des poudres, tel qu'on observe dans les essais de brève durée à 70°-75°C et celui du matériel conservé à la température ambiante pendant de longues périodes.

Des pressions de 25 g/cm² appliquées à des échantillons maintenus à 55°C pendant 20 heures, selon les normes requises pour le traitement avant emmagasinage dans des conditions tropicales, n'ont eu que peu d'effet. A haute pression, l'aptitude à se mettre en suspension est en fonction inverse du logarithme de la pression. Elle diminue lorsque la pression augmente, mais indépendamment du temps pendant lequel s'exerce la pression.

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