Comparison of Suspensibility Test Methods for Water-Dispersible Insecticide Powders

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Five methods of suspensibility testing as found in prominent specifications are compared for the purpose of correlating the efforts to supply suitable criteria of physical quality. The common effect of the methods is to ensure that under rigorous conditions not much of the material in a given powder shall have settling velocities greater than about 1 cm. per minute. The recognition of this as the specific objective is suggested as a focal point for coordination of further development in test methods. It would be advantageous to introduce such coordination now, while interest in the high-suspensibility type of powder for agricultural applications is in the incipient stage.

FOR SEVERAL YEARS importance has been attached to the manufacture of a type of water-dispersible insecticide powder differing from that in common use in this country with respect to ease of settling out from suspension. This has been occasioned by the wide range in efficiency of agitation in present-day application equipment. Power sprayers and some hand-operated ones are equipped with automatic agitators; with simpler equipment the instructions call for occasional stirring, shaking, or tumbling to resuspend the particles that have settled to the bottom, and restore homogeneity to the whole column. Programs, utilizing large numbers of compressed-air tank sprayers and bucket pumps without dashers, in the hands of untrained operators, have brought forth a demand for powders so slow-settling as to render unessential any agitation after the spraying has begun. There has been diversity of opinion as to the advisability of adopting powders of high suspensibility for general use; yet they have already been used in agriculture, and almost anyone concerned with making, buying, or using wettable powders has reason to be interested in the characteristics of this premium grade.

Because many of the most popular organic insecticides are not easily wetted by water, and not easily pulverized to a finely divided state, it is hard enough to prepare a concentrated water-dispersible powder even to ordinary standards, without the added difficulty of meeting the high suspensibility standards. Although by necessity powders of this type have been in large scale production for several years, their performance has usually been a compromise between the idealism of the consumer and the realism of the formulator. Such standards as existed have been subjected to repeated clarification and revision. This paper compares various criteria that have been used

Table I. Principal Conditions of Five Suspensibility Test Methods for Insecticides

(Hard water used throughout)

Condition	DDT	Dieldrin	BHC I	BHC II	WHO General
Original concentration, %	2.5	0.625	3.85	3.85	Depends on toxicant
Sedimentation vessel	100-ml. graduated cylinder	250-ml. graduated cylinder	100-ml. Crow receiver	Graduated cylinder	250-ml. graduated cylinder
Temperature, ° C.	30 or indefinite	10 and 30	20	20	30
Pretreatment	Mild oven or none	None	None; also 1 month at 50° C.	None; also 1 month at 50° C.	Mild oven
Effective sampling depth, cm.	7	10	0–15	0–14	0–19
Settling period, minutes	30	30	10	10	30
Derived reference velocity, cm./hr.	14	20	0–90	0–84	0–38
Minimum final relative concentration, % of original	48–80, usually 60	70	75	65	50

for judging the suspensibility of slow-settling powders, and interprets them on a common basis.

Each of the test methods involves some kind of observation of settling rate, and so may be considered a sedimentation procedure. However, the approach is different from the usual sedimentation work. Sedimentation studies frequently take the form of particle size investigations, settling-rate measurements being used to calculate particle size distribution. Where particle size is the center of interest a knowledge of the relationship between size and settling velocity is useful, despite its complications and limitations. These complications would be a particularly serious handicap in the present case, because of the wide difference in specific gravity between active ingredient and

carrier, and also because the conditions in practical use under which it is desirable to test the sample, with respect to temperature, concentration, and water hardness, may not always produce the thorough dispersion necessary for determination of ultimate particle size. Fortunately, it is not necessary to express the results in terms of particle size, for the real interest here is in settling rate *per se*, and only under the conditions of use.

As any normal sample of powder contains particles of many sizes, a comprehensive sedimentation analysis consists of a detailed evaluation over a range of sizes or settling rates, usually from zero to a practical maximum limit. The results are commonly presented graphically, and the most useful form of graph is the cumulative distribution curve.

This curve provides a universal language into which the empirical terms of the various suspensibility tests may be translated, as is done for the present comparison.

Test Methods

The test methods compared are five in number, though in some cases what is counted as a single method has appeared in several modifications and under more than one name. The principal features of each method are given in Table I. The original concentration percentages are on a weight-per-volume basis (grams per 100 ml.). The water used is a hard water prepared by various procedures, but it always contains 304 mg. of calcium chloride and 65 mg. of magnesium chloride per liter (anhydrous basis), the equivalent of 342 p.p.m. calculated as calcium carbonate.

The first method, designated as the DDT method, though it has been considered for formulations of other toxicants, is represented by the well-known World Health Organization Specification No. WHO/SIFORM/1, for DDT water-dispersible powder concentrates (50% and above), approved Dec. 4, 1951 (4). Here the minimum final relative concentration requirement is 60% of the original; an earlier form of the WHO specification (3) had a requirement of 80% (except for formulations containing 90% of DDT in the dry powder). In both specifications the suspension was prepared from powder taken directly from stock—that is, without pretreatment. Concurrent with the use of actual WHO specifications there were adaptations of this method in which the preparation of suspension was preceded by a mild oven treatment at 55° C. for 24 hours (later changed to 20 hours for convenience of routine operation), with an added-weight pressure of 25 grams per square centimeter. The added weight

corresponds to the weight of powder over a spot somewhere near the bottom in a typical shipping drum. The Foreign Operations Administration (now the International Cooperation Administration) (2) used this method both with and without pretreatment, allowing a lower final relative concentration (48%) under the former condition. In all forms of the method the final concentration is evaluated by analysis for DDT.

The dieldrin method (7) is similar to the DDT method, but the test is done on a larger scale, and without pretreatment.

The BHC methods, I and II, are from specification No. WHO/SIFORM/2, for benzene hexachloride water-dispersible powder concentrates (50% technical benzene hexachloride and above), approved Dec. 4, 1951 (1). They differ from the foregoing in that the final concentration derivable is the average of practically the entire length of the suspension column. The two BHC tests are so much alike as to render questionable the value of performing both on the same sample, except for purposes of study.

The WHO general method (5), adopted in September 1954, is similar in principle to BHC method II. The sedimentation test is done with pretreatment of the mild oven type used in the DDT method. Final concentration is evaluated by chemical analysis. The sedimentation procedure is essentially a revival of an earlier procedure used by WHO (3) for DDT with pretreatment under hot humid conditions (4 weeks at 35° C. and 85% relative humidity).

Aspects of Velocity-Distribution Curve

The cumulative settling-velocity distribution curve for a typical powder of the high-suspensibility type is presented in Figure 1. Such a curve is derived by making a succession of concentration

determinations at different times and/or depths, and filling in between the observed points by interpolation. In some methods the observation can be practically continuous. The finished curve constitutes a condensed reference file, from which can be read off any particular settling-rate characteristic of the sample that interest demands. Point A, for example, shows that 80% of the sample
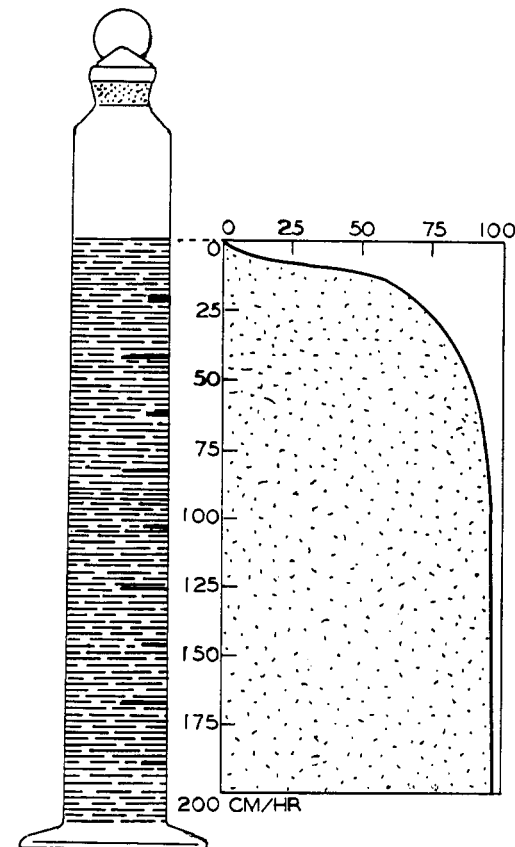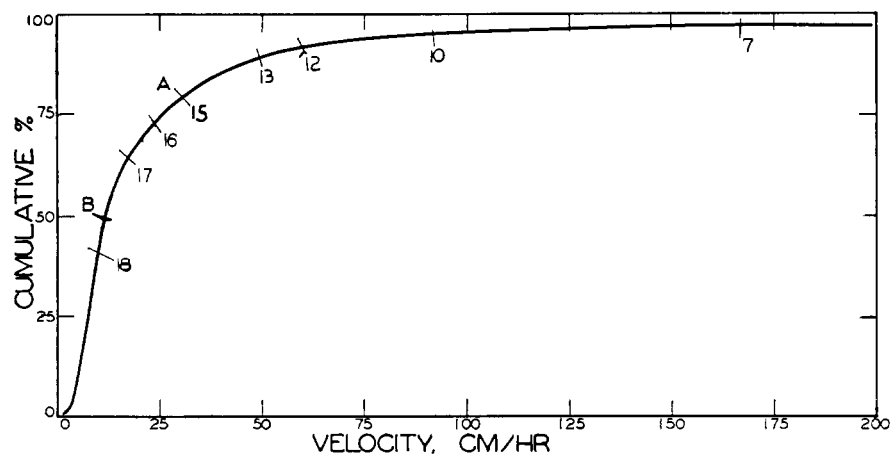
Figure 2. Relation between cumulative settling-velocity distribution and concentration distribution

Width of shaded strip at any level represents concentration at the same level, at end of a certain settling time (unit time X vertical scale of graph)

is slower than 30 cm. per hour, and point B shows that the mass median velocity is 11 cm. per hour.

Such information is hardly more than academic, unless there are visible the details of its linkage with the behavior of the powder in suspension during the spraying operation. To assist our visualization let us rotate the graph clockwise through 90°, to the position in Figure 2. Here the graph is standing alongside a cylinder containing a suspension of the powder. The zero point is on a level with the surface of the liquid, the velocity axis now serving as a kind of depth gage. The area under the curve is shaded to facilitate its visualization as a vertical strip varying in width. The graph now becomes a "life-size" picture of the suspension at some moment, the

Figure 1. Cumulative settling-velocity distribution of typical high-suspensibility powder

A. 80% level
B. Mass median velocity
Numerals on curve relate concentration to spraying time in a specific example

width of the strip at any given level being the relative concentration at that level. Furthermore, the graph contains the key to two extensions of this bit of information. First it enables us to tell after how long a settling period the condition of the spray suspension will be as here pictured. Second, it enables us to draw a whole series of views, like the frames of a movie film, showing how the picture changes from minute to minute throughout any reasonable settling time.

It is obvious that the simple question—how soon will the powder settle out—has no simple answer. In the settling-velocity distribution curve, however, can be found the answers to any specific elements of the question, one at a time.

This relationship between the velocity-distribution curve and the changes in concentration distribution during the settling period is based on the familiar sedimentation principle that at any given elapsed time (say 1 hour) a thin layer of the suspension at any given depth (10 cm.) will contain just as much of every size and kind of particle as it had in the beginning, except that it will have lost all particles falling fast enough to go from the top to beyond the given depth in the given time (faster than 10 cm. per hour). Therefore, if at the end of an hour the concentration at 10-cm. depth is 40% of the original concentration, the velocity of this percentage of the sample is less than 10 cm. per hour, and so on for the whole range of depths. Now with the graph used as a depth gage as in Figure 2, if the velocity units are on the scale of actual lengths per hour (so that

1 cm. represents 1 cm. per hour), then the shaded strip will indicate directly the respective concentrations at all depths as found at the end of a 1-hour settling period. Similarly, if the velocity axis is drawn to one third this scale (1 cm. = 3 cm. per hour), the picture will be that of the concentration at the end of 20 minutes, to one half scale for 30 minutes, etc.

Such a time series based on the curve of Figure 1 is shown at intervals of 10 minutes in Figure 3, illustrating a suspension standing unused in a compression sprayer. This depiction ignores the slight inequality of cross section caused by the pump cylinder extending only part way through the liquid.

To this point the illustrations have shown only simple cases where the suspension is standing without use. What happens to the concentration distribution while spraying is in progress? In any spraying operation, even in those employing the most passive procedures, the particles are subject to changing conditions not encountered in the usual laboratory tests, including fluid disturbances from one cause and another not intended for remixing. Some of the unregulated influences acting within the cylinder of a compression sprayer or the pail of a bucket pump will be helpful and some a hindrance. As far as straight settling is concerned, the analysis is essentially the some as for a stationary liquid column, except that each successive sampling is done not only after a longer settling time but also at a lesser depth. Instead of thinking of the water level as subsiding in

the reservoir, we may consider the discharge-line inlet at the floor of the reservoir as a continuous sampling device moving upward through the liquid column. Take for example, a vertical-sided vessel filled to a 30-cm. (1-foot) depth with freshly stirred suspension, and a constant spraying rate adjusted to empty the vessel in 20 minutes. At the beginning the spray will be coming from a depth of 30 cm., after no settling time, so that the relative concentration in the delivered spray will be 100%. After 2 minutes the depth will be 27 cm., so that the maximum settling velocity of particles in the delivered spray will be 27 cm. per 2 minutes, or 810 cm. per hour, far off the scale of our graph (Figure 1). Six minutes of spraying will take us almost into the graph at the right-hand edge (200 cm. per hour), where for the sample here represented the relative concentration in the delivered spray is still better than 95%. From here on the curve is marked at several places to designate the minutes of elapsed settling time in this experiment. It will be noted that the concentration keeps above the 90% level until sometime in the 13th minute, and above 80% to the end of the 15th minute, when we are drawing from a layer 7.5 cm. (3 inches) from the surface. From here on the drop in concentration is rapid.

Thus it is seen that in ordinary use—i.e., spraying promptly after mixing but with no agitator in the sprayer tank—a high-suspensibility powder tends to hold its concentration fairly near its original value until a minor fraction of the load
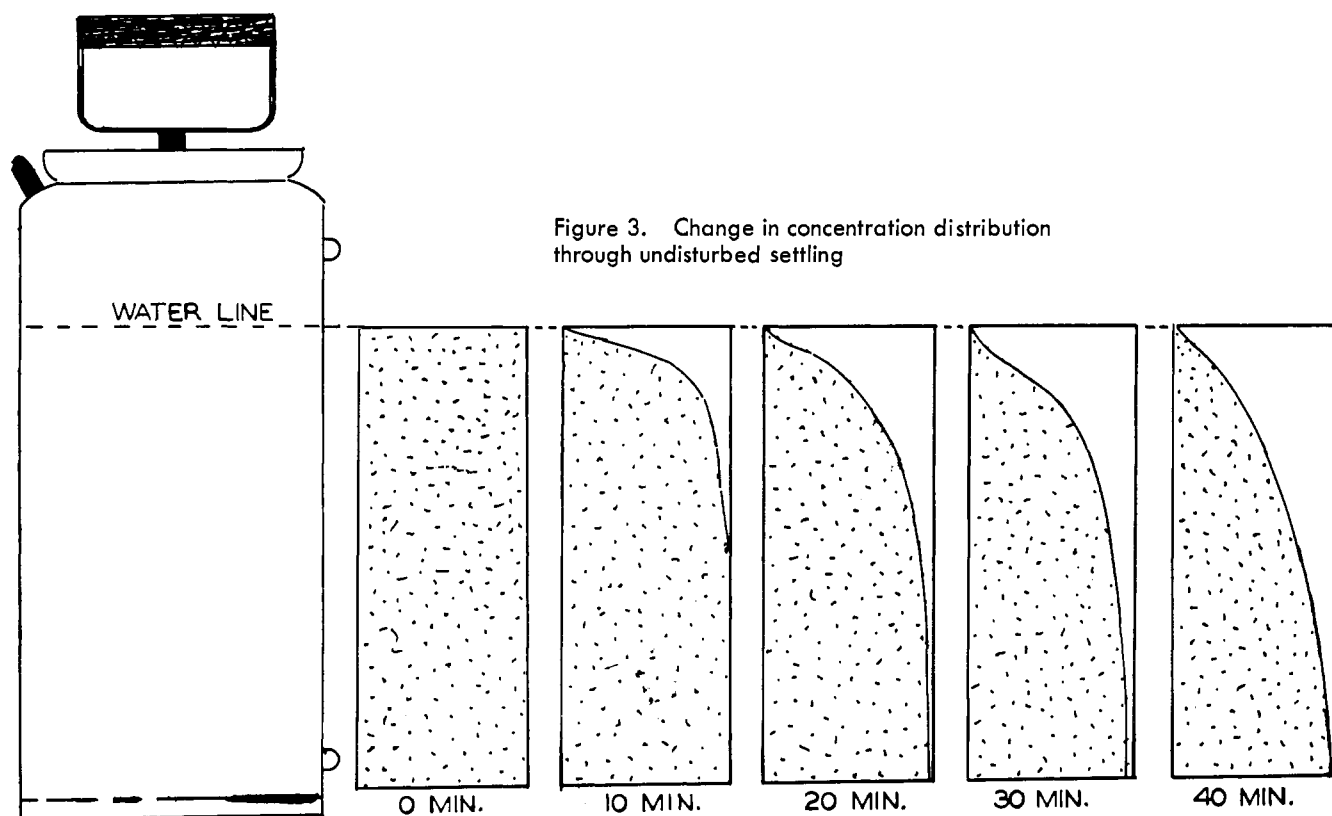

Figure 3. Change in concentration distribution through undisturbed settling

WATER LINE

0 MIN.   10 MIN.   20 MIN.   30 MIN.   40 MIN.

remains in the tank. The function of the specification test is to make sure that this fraction is small, which will not be the case unless the powder is produced specifically for the high-suspensibility market. The high-suspensibility type powder has a phase near the end of the spraying where the concentration theoretically decreases rapidly to zero; nothing can be done about this except to reagitate the suspension at or before the approach to this period.

In order to simplify the analysis in the foregoing example, the conditions were closely regulated. No settling period was allowed before the beginning of spraying. If this occurs there will be an initial deposit at the bottom near the inlet to the spray tube, and the magnitude of this deposit will be represented by the unshaded area in the appropriate picture in Figure 3.

Furthermore, in this example the volume rate of spray delivery was kept uniform. With hand-pumped compression sprayers there is commonly a rapid decrease of pressure near the beginning, due to the small size of the original air space. For this reason the volume delivery rate begins to lag while the rate of deposition of sediment is still near its original and maximum value, so that there is a tendency for the delivery concentration peak to occur after spraying has continued for a short while, instead of at the start.

Application of Curve to Test Methods

With this background we are ready to interpret each of the test methods in terms of settling velocity. For this purpose the original curve (Figure 1) is reproduced in Figure 4. In all five methods many procedural details have been omitted, because the purpose of this comparison is interpretation of the essentials, rather than criticism.

DDT Method. The 100-ml. graduate used as a sedimentation cylinder in this test has a scale depth of 18 cm., and a 25-ml. sample is taken by means of a pipet, introduced at the end of the settling period, with the tip at the 50-ml. mark (9-cm. depth). Therefore, neglecting the undercutting caused by tendency to streamline flow around the pipet tip, we may regard the sample as consisting of the second quarter (measuring from the top) of the whole suspension column, covering the depth range 4.5 to 9.0 cm. The settling period is 30 minutes. Thus, the sample whose overall concentration is to be determined is essentially a composite of successive layers representing all maximum velocities from 4.5 to 9 cm. per 30 minutes, or 9 to 18 cm. per hour. This is the range A to D in Figure 4. Although for any given sample the curve in this region may not be sensibly straight, careful study will show that the average height over this

range can hardly be much different from the height at the middle velocity. Therefore, we may refer the average concentration of the pipet sample to the middle of the velocity range, which, with a small allowance for the undercutting, may be rounded off to 14 cm. per hour.

Figure 4. Curve in Figure 1, showing portion covered by each test method

Sampling ranges
DDT method, A to D, with effective velocity as at B
Dieldrin method, C to F, with effective velocity as at E
WHO general method and BHC methods I and II, from 0 to G, J, and H, respectively

Thus the specification minimum requirement of 60% for the relative concentration in the pipet sample amounts to 60 per cent under 14 cm. per hour. This minimum coincides with point B of the graph.

Dieldrin Method. In this test the cylinder volume is 250 ml., the scale depth 24.0 (±1.5) cm., the pipet sample volume 50 ml., the pipet tip depth approximately 12 cm., the settling period 30 minutes, and the minimum final relative concentration requirement 70% (based on analysis for active ingredient in suspension). Calculating and rounding off as before converts the effective sampling depth to 10 cm. and the minimum requirement to 70% under 20 cm. per hour. On the graph the range of maximum velocities is approximately C to F, and the minimum requirement coincides with point E.

BHC Method I. This method differs from the preceding ones in two major respects: (1) The ranges of depth and velocity involved in the observation begin at zero, and (2) the evaluation is based on apparent volume of sediment. The sedimentation vessel is a 100-ml. Crow receiver, conforming in dimensions to British Standard Specification No. 605. The receiver is not strictly cylindrical, being tapered near the bottom for sensitivity of sediment volume reading. Because of this and certain other features of the procedure, it is impossible to state the effective depth range exactly, but in any normal case it will be approximately 15 cm. This with the

settling time of 10 minutes reduces to a maximum velocity of 90 cm. per hour. The relative measure of sediment is calculated by reference to the amount accumulated in 48 hours, which may be assumed to constitute the entire or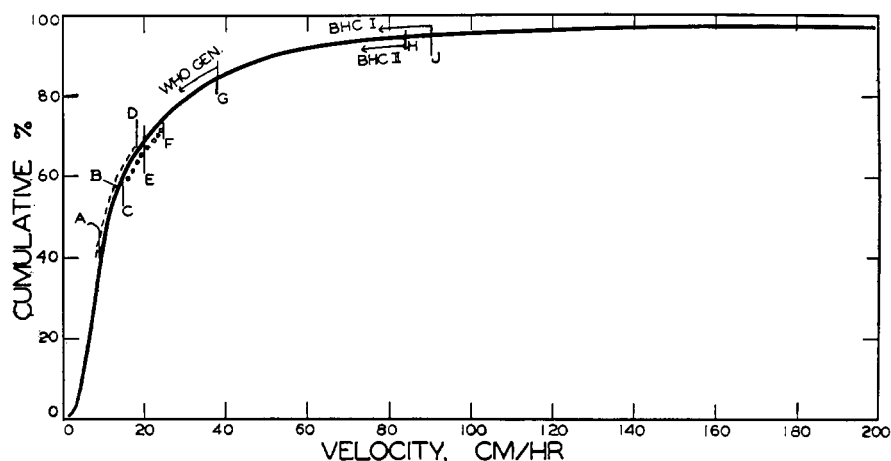iginal sample. Observation of the percentage settled out in 10 minutes establishes by difference the percentage still in suspension, but over the entire range (0 to 15 cm.). The maximum acceptable sediment is 25%. The final relative concentration is essentially a composite of the cumulative percentages under all successive velocities from 0 to 90 cm. per hour. It will be apparent from the graph that with this long range of velocities we should hardly be justified in splitting the difference, as in the previous methods, to arrive at a single reference velocity. The most specific interpretation of the requirement is that the average height of the curve from the origin to J must be not less than 75 per cent. The case illustrated meets this requirement with an ample margin.

BHC Method II. This is similar to the preceding BHC method, the principal differences being that the vessel is an ordinary graduated cylinder and the evaluation of sediment is done by chemical analysis after removal of the liquid layer. The cylinder is of unspecified volume, but filled to a depth of 15 cm., thus providing a liquid depth of about 14 cm. at the end of the 10-minute settling period. Interpretation analogous to that for method I expresses the requirement that the average height of the curve from the origin to H shall not be less than 65%.

WHO General Method. The principal differences between this type of procedure and that of BHC II are in the dimensions of the apparatus, the settling time, and the water temperature.

The cylinder is a 250-ml. graduate, with scale depth approximately 21 cm., and the uppermost nine tenths of the volume is removed after the 30-minute settling period. For compliance with the specifications, the average concentration in the withdrawn layer must be at least 50% of the original. For convenience the concentration is derived from analysis of the 25 ml. of suspension and sediment remaining in the bottom of the cylinder.

The difference in water temperature makes the viscosity 20% lower than in BHC I and II, so that for accurate comparison the settling velocities should be adjusted to a common temperature. However, because of the uncertainty of effects of temperature on floccule size, and the fact that in some of the other procedures the temperature is indefinite, no attempt will be made to correct for viscosity differences.

The original concentrations for the general method are varied to suit the active ingredient. The percentage concentration for DDT, chlordane, malathion, and methoxychlor is 2.5; for dieldrin 0.625; for BHC 0.5, based on gamma isomer content only; and for Diazinon also 0.5.

In velocity range the general method presents a compromise between the relatively narrow bands of the DDT and dieldrin methods and wide range of the BHC methods. The new range is 0 to 19 cm. in 30 minutes, or 0 to 38 cm. per hour. The specification requirement means that the average height of the curve over the range from the origin to G shall be not less than 50%. The sample represented meets this requirement, with a little to spare.

Discussion

The high-suspensibility type of water-dispersible insecticide powder is one in which nearly all components have settling velocities no higher than the order of 1 cm. per minute. In this connection velocity is not expressible in terms of a specific particle size, but is a characteristic of prime interest for itself alone. In terms of the cumulative settling-velocity distribution curve, this means a high plateau beginning in or before the vicinity of 60 cm. per hour.

Each of the specification test requirements seeks in its own way to bolster the curve by supporting it at some place in or preceding this vicinity. The DDT and dieldrin methods tackle the curve at fairly definite points, the former holding the percentage up to 60 (usually) at 14 cm. per hour and the latter to 70 at 20 cm. per hour. The BHC methods (I and II) and the WHO general method use a more generalized approach, maintaining a minimum average height over roughly the entire preplateau region; the minimum average heights (cumulative percentages) and the ranges over which they are ensured by the respective methods are 75% from 0 to 90 cm. per hour, 65% from 0 to 84 cm. per hour, and 50% from 0 to 38 cm. per hour.

The way in which these diverse methods fit together into a pattern suggests what may be a more direct approach to their common purpose. In terms of guarantees for effective life of unreagitated suspension, these methods act by regulating various features of the final sharply deteriorating phase. One wonders if it would not be simpler and equally effective to regulate this

unsatisfactory phase merely by making it as brief as possible. Instead of stipulating how low a level of performance will be tolerated at certain stages of the failure period, or in overall average for this period, we might set a minimum limit on duration of good performance, ignoring the details of the unavoidable drop at the end. The criterion would be established with regard to the shoulder of the curve. A suggested requirement based on this aspect is not less than 90%, under 60 cm. per hour.

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AMMONIUM METAPHOSPHATE FERTILIZER

Pilot Plant Production and Greenhouse Tests of Fertilizer from Ammonia and Phosphorus Pentoxide Vapors

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PRODUCTION OF A CONCENTRATED NITROGEN-PHOSPHATE FERTILIZER directly from ammonia and phosphorus pentoxide was studied by the Tennessee Valley Authority as a part of its search for new and improved fertilizers. The work resulted in the development of a process for the production of a fertilizer containing 90% plant food (17% nitro-

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gen and 73% phosphorus pentoxide). The process consists of burning phosphorus with dried air, making the resultant gas containing phosphorus pentoxide vapor react with ammonia at elevated temperatures, and hydrolyzing the product from this reaction with steam.

Other investigators also have studied the reaction of ammonia and phosphorus pentoxide. Ross, Merz, and Carothers (8) reported the production of a fer-

tilizer from the reaction of ammonia and phosphorus pentoxide in the presence of water but did not give sufficient information to permit defining the requirements of the process. The product obtained in their investigation was a light, fluffy powder, and they postulated that it was a mixture of ammonium metaphosphate, ammonium orthophosphate, and ammonium pyrophosphate. Rice (6, 7) also published information on the reaction of ammonia and phosphorus