zone of viscosity that coincided with the first and partial appearance of gel formation was in the range of magnitude of 90 to 100 cps.

As gelation progressed but was still in the stage so that a uniform fluidity would be obtained by pouring milk back and forth, viscosity increased to 150 to 200 cps. Beyond this stage of gelation the milk was lumpy after mixing and the viscosity values were in the range of several hundred centipoises. Viscosity measurements of heat-processed products like evaporated milk represent only relative values. It is not absolute viscosity, because there is yield value or structure even when product is entirely fluid and some of the structural viscosity is destroyed by mixing. These relative viscosity values, however, do reflect the consistency of the body of the product and are suitable for comparative purposes.

The data in Figures 1 to 4 show the general behavior of various concentrated milks in storage with respect to viscosity, and the marked retardation of gelation by certain preheating treatments of milk in a concentrated state.

The data of Figure 1 show that a more severe heat treatment (13 minutes at 243° F.) with conventional sterilization ensures the fluidity of milk in storage. The shelf life of HT-ST sterilized milks is limited by gelation, varying undoubtedly with differences in the colloidal properties of the original milks. Figure 2 illustrates that the rate of gelation in storage is a function of milk solids concentration. In separate experiments it was shown that the accelerated rate of gelation with increased concentration is entirely associated with increased concentration of solids-not-fat fraction. This can be seen also by comparing the rate of gelation of concentrated whole and skim milk controls in Figure 3.

The effectiveness of preheating milk in a concentrated state on the rate of gelation in storage of HT-ST-sterilized milk is shown in Figures 3 and 4. The data of Figure 4 indicate that preheating milk in the concentrated state before sterilization controls the gelation defect of HT-ST–sterilized evaporated milk. In other experiments milk was concentrated to contain 40% total solids, and the samples made by dilution and containing from 40% to 28% total solids were preheated. The preheated samples were all diluted to standard composition (26% total solids) and sterilized. The data on gelation of these samples in storage indicated that the optimum time and temperature of preheating treatment will vary with the concentration of the milk at the time it is preheated. For example, at 28% total solids, preheating treatment at 195° F. for 30 minutes gave greater retardation of gelation than preheating at 180° F. for 30 minutes, but at 35% total solids, the indicated optimum treatment was preheating at 180° F. for 30 minutes. At higher concentrations, preheating treatments of lesser severity are required for optimum retardation of gelation in storage.

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**PESTICIDE ANALYSIS**

# Determination of Captan


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**A specific and sensitive analytical method for the fungicide, captan, *N*-(trichloromethylthio)tetrahydrophthalimide is based on the reaction with alkaline resorcinol under reducing conditions. The method is most useful in the range of 3 to 30 γ, and a semiquantitative measure of as little as 0.4 γ is readily obtained. Good recoveries were obtained from various natural products.**


Reactions of molten resorcinol with compounds containing the $-CCl_3$ group were investigated during work on analytical methods for chlorinated hydrocarbon pesticides, as these might be expected to give fluorescein derivatives (*3*). An example of such a reaction appeared in the analytical method developed by Kittleson (*4*) for the commonly used fungicide, *N*-(trichloromethylthio)tetrahydrophthalimide (captan) (*7*). It was found that certain of these pesticides gave fluorescein-like derivatives, and that the liberated hydrochloric acid contributed to the color formation. In alkaline medium, only captan gave a significant color with resorcinol. Addition of sodium hydrosulfite to the alkaline resorcinol minimized interference from air oxidation, making this a highly sensitive and specific analytical reagent for captan determination. This appears to have some advantages over the Kittleson method (*2, 4*), the only other method available.

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### Experimental

**Preparation of Sample.** For firm-surfaced materials, the usual methods for stripping pesticides from the surface of food products appear to be suitable. Experiments have been carried out with apples, pears, tomatoes, and whole wheat. They were agitated with benzene for 5 minutes, the solvent was filtered through folded filter paper, and an

aliquot was taken for analysis. Methods which have been recommended (*2*) for blood, milk, meat, and body fat should be equally applicable.

**Reagents.** All chemicals used are analytical reagent grade.

Acetone.

Sodium hydrosulfite.

2*N* sodium hydroxide. Stored in a polyethylene bottle.

Methanolic Resorcinol. Place 12.5 grams of resorcinol in a 100-ml. volumetric flask and make to volume with methanol. The solution is usable for several weeks when kept in a refrigerator.

**Procedure.** Evaporate a portion of the strippings from the captan-bearing sample to dryness, and take up the residue in a volume of acetone so that 1 ml. will contain from 3 to 30 γ of captan. Place 1 ml. of this acetone solution in a small 12 × 75 mm. test tube, and stopper the tube tightly.

Dissolve about 15 to 20 mg. of sodium hydrosulfite (a home-made measuring spoon is convenient) in 2 ml. of 2 *N* sodium hydroxide in an ordinary test tube. Add 2 ml. of methanolic resorcinol. Since the methanolic resorcinol tends to layer on top of the sodium hydroxide, mix these reagents thoroughly. Pour the reagents into the captan test tube, and pour back and forth twice. Stopper and store in the dark. Read the absorbance in a Beckman DU spectrophotometer at 447 and 500 mμ at least 12 minutes after mixing, but not more than 1 hour after. Water was used to obtain the zero setting as a reference point. An air path will also serve.

The absorbance due to captan is taken as the difference between the reading at 447 mμ and that at 500 mμ, the latter reading serving as an internal blank. The above procedure is followed for a series of standard captan solutions in acetone in the range from 0 to 30 γ per ml., and a standard curve is prepared. A recheck on the standard curve is necessary only occasionally, unless high precision is sought in the determinations. A filter colorimeter such as the Klett-Summerson may be used instead of a spectrophotometer, with some sacrifice of precision. A 440-mμ filter was found to be satisfactory. A captan-free sample of the same material as that being analyzed must be carried through the entire procedure. This constitutes a blank, whose colorimeter reading is subtracted from that of the experimental material.

### Comments on Procedure

A number of conditions may lead to the appearance of a precipitate in the final reaction mixture. Most of the conditions are avoidable, so that clear solutions can always be obtained with the standard captan solutions. However, samples prepared from natural materials occasionally contain materials which give rise to more or less turbidity. A degree of turbidity small enough that the readings remain on the useful part of the spectrophotometer scale will ordinarily not be serious, as the absorbances at 447 and 500 mμ will be increased to approximately the same extent. An objectionable amount of precipitate can usually be removed by centrifuging.

Sodium hydrosulfite was added to prevent air oxidation which results in a dark green color forming at the surface of the final reaction mixture. The amount of hydrosulfite was not critical, as the same net readings were obtained when the amount was varied between 10 and 40 mg. However, when 40 mg. or more was used, a precipitate appeared in the final reaction mixture, presumably because the limit of solubility of the hydrosulfite had been exceeded. The greenish discoloration appeared more quickly as a result of agitation of the solution after mixing was completed, when the surface exposed to the air was increased, or when the amount of hydrosulfite was decreased. Hence, if a larger test tube than that recommended is used—e.g., a Klett-Summerson colorimeter tube—the amount of hydrosulfite used should be increased.

The concentration of sodium hydroxide is not critical, as can be seen from Figure 1 where the net readings for 10 γ of captan are plotted for various alkali concentrations. The use of sodium hydroxide solutions which had stood in glass containers until they contained excessive amounts of sodium silicate resulted in the appearance of a precipitate in the final reaction mixture. The alkaline sodium hydrosulfite should not be allowed to stand unnecessarily before proceeding with the addition of reagents. When the addition of methanolic resorcinol was delayed for 30 minutes, precipitation occurred in the final solution.

The concentration of resorcinol is not critical. The amount of color was not significantly changed when the concentration of the methanolic resorcinol solution was changed over the range of 20 to 10 volume %, but at lower concentration there was less color. The absorbance was greater when the solvent for the resorcinol was methanol rather than ethanol. The order of mixing has some importance, as somewhat less color was obtained when the acetone solution of the sample was added to the mixed reagents first.

The yellow-colored reaction product fades rapidly if left in the light, from which it should be protected as soon as mixing is completed, except for necessary operations such as transfer to the cuvette. Exposure to the spectrophotometer light beam during readings appeared to have no effect, however. The color appeared immediately on mixing, but the net absorbance increased to some extent during the first 9 to 12 minutes, and then

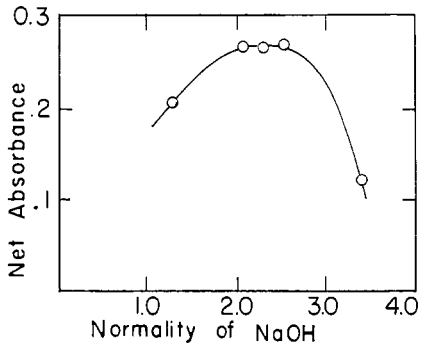


**Figure 1. Effect of sodium hydroxide concentration on color development**

remained constant for at least the next hour. Eventually the net absorbance increased again, owing to the appearance of the green oxidation product. The increase began shortly before the discoloration became obvious to the eye. In some cases the discoloration had not developed until after some hours, but the time of change was erratic and not to be depended on.

The shapes of the absorption curves for several levels of captan (Figure 2) show that the points of maximum and minimum absorbance are at longer wave lengths than the corresponding points on the curve given by Kittleson (*4*). The maximum under these conditions falls at 447 mμ, while the absorbance at 500 mμ is unaffected by the amount of captan. A typical standard curve is given in Figure 3.

**Possible Interfering Substances.** A large number of pesticides [named here as they are listed in (*1*), where more precise descriptions are given] have been investigated for possible interference. The following gave no significant net absorbance under the conditions of this method, when 500 and 600 γ was present in the final mixture: DDT, 2,4-D, lindane, benzene hexachloride, dichlorodiphenyldichloroethane, methoxychlor, chlordan, toxaphene, dieldrin, aldrin, dilan, heptachlor, rotenone, and 2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethylene (DDE). This amount of these pesticides would represent at least a 20-fold excess as compared with the amount of captan. The solubility of hexachlorobenzene in this system is limited, but 240 γ gave no significant net absorbance. The only pesticide giving any detectable interference was spergon (chloranil). In this case, 90 γ of spergon gave a reading on the standard curve equivalent to about 1.5 γ of captan, and 500 γ of spergon was equivalent to about 5.5 γ of captan.

**Sensitivity and Precision.** An experiment was carried out to determine the limit of sensitivity of the method with 1-cm. glass cuvettes not specially matched. The results given in Table I

indicate that the method can give a semi-quantitative measure of 0.4 γ of captan under these conditions. With more careful technique, or with a longer light path in the cuvette, greater sensitivity would be possible.

The reproducibility of the procedure is indicated by the close fit of the points in Figure 3. Further evidence on this point is supplied by the data in Table II. It is evident that the variability in the analytical procedure is small as compared with sampling variation.

### Recovery Experiments

Recovery experiments have been designed in several ways. Those listed under Type A in Table III were carried out by stripping the untreated product with benzene according to the procedure described in the first part of this paper, and evaporating an aliquot to dryness. The residue was then taken up in an acetone solution of captan of known concentration, such that the amount of captan simulated a reasonable residue level on the food product, and the amount of acetone gave a concentration falling on a useful part of the standard curve.

In the experiment listed as Type B, a uniform suspension of a 40% captan–40% hexachlorobenzene wettable powder in water was made. Eighteen tomatoes were dipped in this, drained for a short time, and allowed to dry. An aliquot of the suspension was dried, taken up in acetone, and analyzed. From the initial and final weights, it was found that the initial amount of captan was 45.0 mg. and the final amount was 41.61 mg. The equipment used for dipping and drying the tomatoes was washed with acetone. Analysis showed that 1.55 mg. of captan was lost in this way. The tomatoes were stripped with benzene in the usual way, and the strippings were found to contain 1.95 mg. of captan, as compared with the calculated amount of 1.84 mg.

For experiment C, the captan content of the wettable power itself was determined, by analyzing a filtered acetone solution. A figure of 39.9% was obtained. A small volume of a suspension of the wettable powder of known concentration was evenly distributed over a sample of whole wheat by shaking them together in a flask. The amount of captan calculated to have been applied to the wheat was 0.873 mg. and the amount found in the strippings was 0.895 mg.

### Discussion

The use of an internal blank has several advantages over the use of a separately prepared solution. All the spectrophotometer cuvettes may contain actual samples. The time of preparation of a blank is saved. There is automatic compensation for resorcinol color and for absorption due to occasional variable turbidity or precipitation.

The alkaline resorcinol reagent appears to be less subject to interference from other pesticides than the Kittleson procedure, though such interferences with the latter method are small enough to be negligible ordinarily. Comparisons of sensitivity are a little uncertain. The standard curve shown in the original Kittleson procedure (*4*) showed 50% transmittance at about 240 γ of captan.

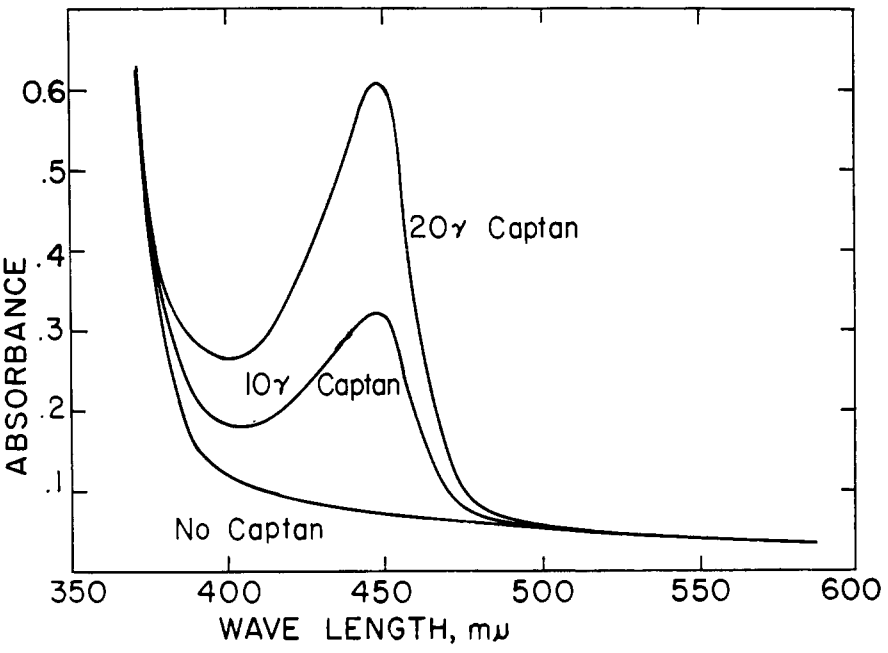


Figure 2. Absorption spectra for reaction products in analytical procedure for captan

**Table I. Absorbance of Small Amounts of Captan**

| Amount of captan, γ | 0 | 0.1 | 0.4 | 1.0 |
|---|---|---|---|---|
| Net absorbance | 0.028 | 0.032 | 0.036 | 0.052 |

**Table II. Reproducibility of Net Absorbance Readings**

| | Replicate Net Absorbance Readings | | | | | |
|---|---|---|---|---|---|---|
| Tomato strippings + 15 γ captan | 0.379 | 0.378 | 0.376 | | | |
| 10 γ captan (on different days) | 0.261 | 0.261 | 0.273 | 0.265 | 0.253 | 0.262 |
| | 0.252 | 0.257 | 0.267 | 0.269 | ($\sigma$ = 0.007) | |

**Table III. Recoveries of Captan from Food Products**

| Type of Experiment[a] | Product | Equivalent P.P.M. Added | Recovery, % |
|---|---|---|---|
| A | Apples | 10 | 98 |
| | | 8 | 105, 97 |
| | | 6 | 100 |
| | Tomatoes | 6 | 98 |
| | | 4.5 | 105 |
| | Pears | 10 | 99 |
| | | 6.7 | 106, 97.5 |
| | | 5 | 97 |
| B | Tomatoes | 1.15 | 105 |
| C | Wheat | 8.3 | 102 |

[a] See text.

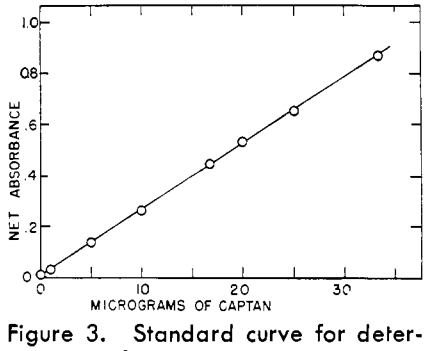


Figure 3. Standard curve for determination of captan

In the modified method (*2*) 57% transmittance corresponds to 50 γ. With the present procedure, 11 γ gives a net absorbance of about 0.3, equivalent to 50% transmittance.


### Acknowledgment

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**PESTICIDE FORMULATION**

# Deactivation of Mineral Carriers for Stable Heptachlor-Dust Formulations


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Because some mineral carriers used in the preparation of dust and granular formulations of heptachlor catalyze degradation of the insecticide, it was desirable to incorporate a deactivator additive in the formulations which would neutralize their activity. Relationships between rate of degradation and temperature, heptachlor concentration, and surface acidity of mineral carriers used were studied. Oxygen-containing chemicals such as diethylene glycol when used in the formulations, were effective in stabilizing the heptachlor.


SOME CHLORINATED ORGANIC INSECTICIDES which are stable in the technical form and in liquid formulations show marked decomposition on certain of the commercial mineral carriers used in the preparation of dust and wettable powder formulations. The extent and rate of decomposition, which are functions of the catalytic activity of the mineral carrier, can be controlled by chemical treatment of the carrier. This discussion is limited to an investigation with heptachlor.

### Materials and Methods

For determining heptachlor stability in various dust formulations and for the screening of possible deactivator additives, the mineral carriers Attaclay, Barden Clay, Celite 209, Pyrax ABB, Emtco, and CCC Diluent (Table V) were chosen as representative of their mineral classes.

Formulations were prepared, usually

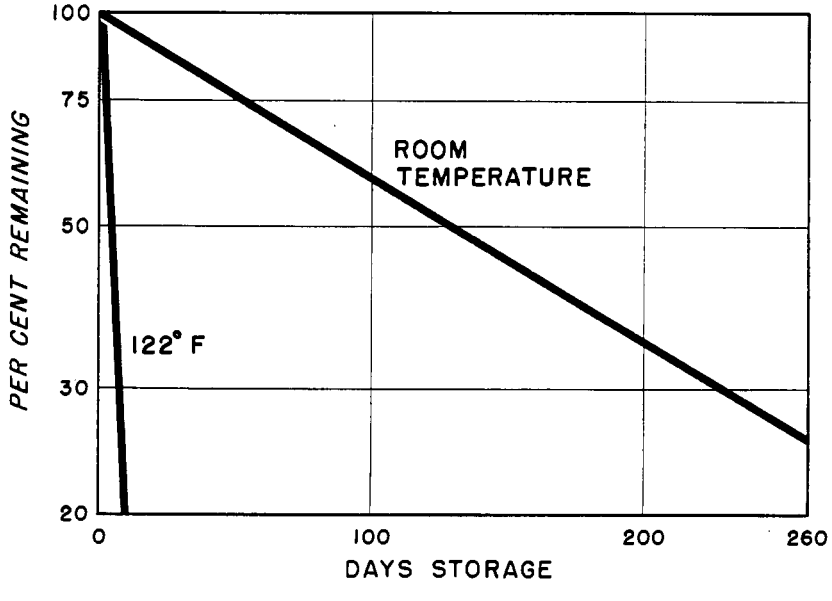


Figure 1. Rate of decomposition of heptachlor on Attaclay