

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

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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

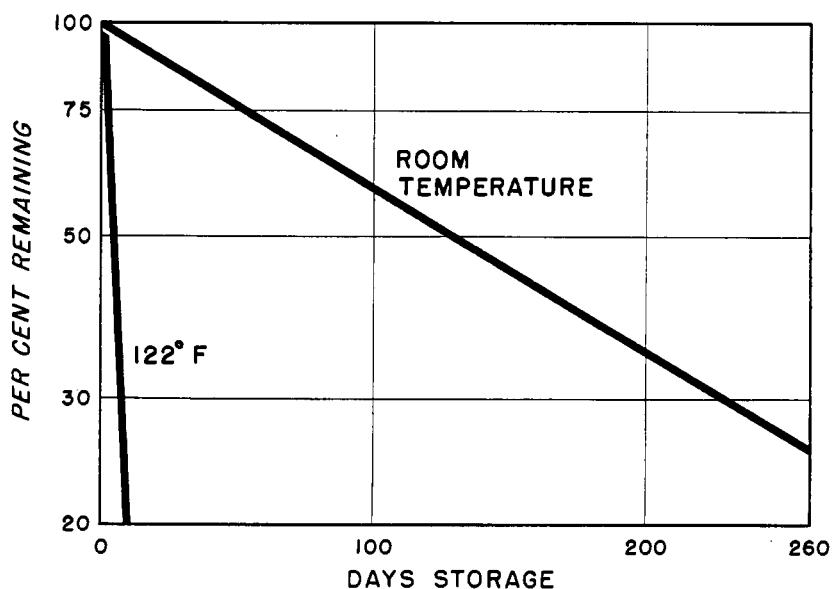


Figure 1. Rate of decomposition of heptachlor on Attaclay

at the 10% heptachlor concentration, by impregnating the carrier with the heptachlor, pulverizing in a hammer mill, and blending in a cone-type blender. In the cases where deactivator additives were tested, the deactivator was intimately mixed with the carrier, both prior to and simultaneously with the addition of the heptachlor.

Storage stability was tested at room temperature and at 122° F. in a thermostated oven. The formulations were stored in sealed glass jars to eliminate the factor of volatilization. The heptachlor content of the formulations was determined by the Polen-Silverman colorimetric method (2) after extraction of the formulation with benzene.

Materials were screened for use as deactivators primarily for ability to stabilize heptachlor formulations, and this information was correlated with the observed reduction of the surface acidity of the minerals tested. Materials which show promise by this criterion should be further screened for such properties as ease of application, volatility, contribution to properties of their formulations, compatibility with other agricultural chemicals, and cost.

#### Correlation of Surface Activity and Stability

The surface acidities of the mineral carriers considered were measured by the method of Walling (3). This technique is based upon the ability of a mineral carrier to convert an adsorbed neutral-base color indicator to its conjugated acidic form. One quarter of a gram of the carrier is placed in a small test tube containing 2 ml. of indicator solution (1 mg. per ml. of iso-octane). The appearance of the color of the acid conjugate indicates a surface acidity greater than the ionization constant (pKa) of the indicator. By using several indicators with different ionization constants, the apparent surface acidity of a carrier can be estimated. A titration technique has been described by which a quantitative measurement can be made (7). The pKa is not equal nor proportional to the pH of an aqueous slurry of the carrier.

The pKa of the various mineral carriers were correlated with the stability

**Table I. Relationship of Surface Acidity to Stability of Heptachlor-Dust Formulations**

Mineral Carrier	Surface Acidity, pKa	Heptachlor Formulation Stability
Attaclay	<1	Poor
Barden clay	<1	Poor
Celite 209	1	Fair
Talc	~3.3	Good
Pyrax ABB	~3.3	Good
CCC Diluent	>3.3	Good

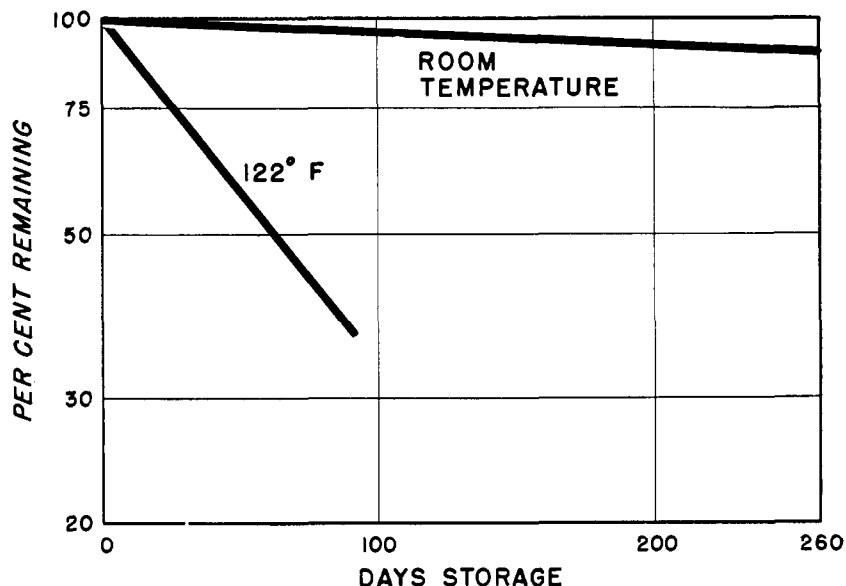


Figure 2. Rate of decomposition of heptachlor on Attaclay-Pyrax (1:9)

of heptachlor when formulated with these minerals (Table I). It is apparent that the carriers which exhibit high surface acidities cannot be used in the preparation of stable formulations without proper deactivation.

#### Rate of Degradation

**Temperature.** The rate of degradation of heptachlor in dust formulations is greatly accelerated at elevated temperatures. Figures 1 to 3 show the decay curves of three formulations stored at 122° F. and at room temperature.

The time at which each formulation reached 90% of its initial concentration

was calculated for the two storage conditions, and the ratios of these times were determined. The average ratio was found to be 38—i.e., 1-day storage at 122° F. is equivalent to 38-day storage at room temperature—so that an accelerated test for 30 days gives results comparable to 3 years' storage under normal conditions. This estimate can be seriously affected by factors other than degradation, such as volatilization of the insecticide. The contribution of volatilization was minimized in this work by storage in sealed glass jars. Since an approximate relationship between normal and accelerated aging was

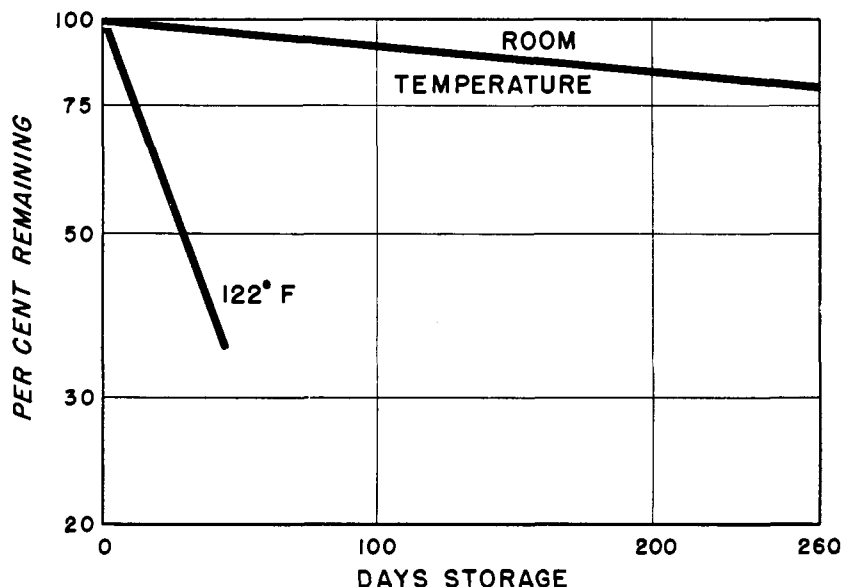


Figure 3. Rate of decomposition of heptachlor on Diatom-Pyrax (1:9)

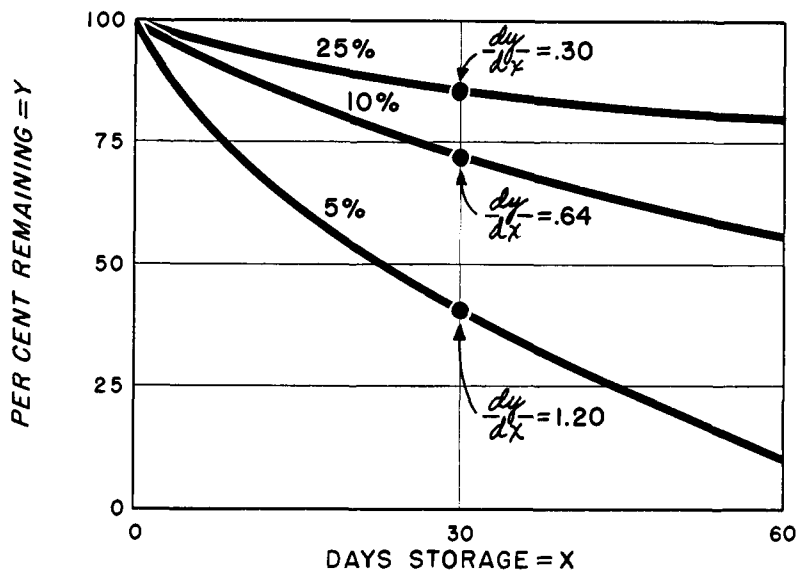


Figure 4. Loss in heptachlor concentration on Celite formulations at various concentrations

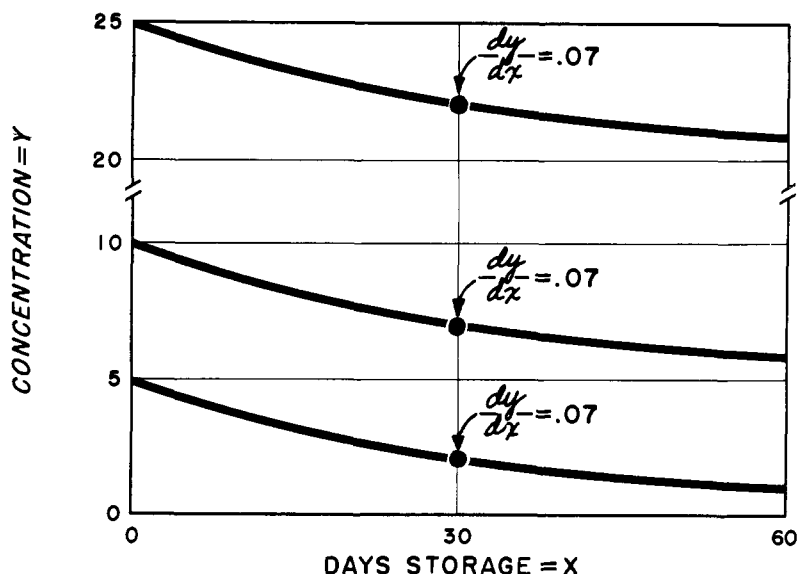


Figure 5. Loss in heptachlor concentration on Celite formulation at various concentrations

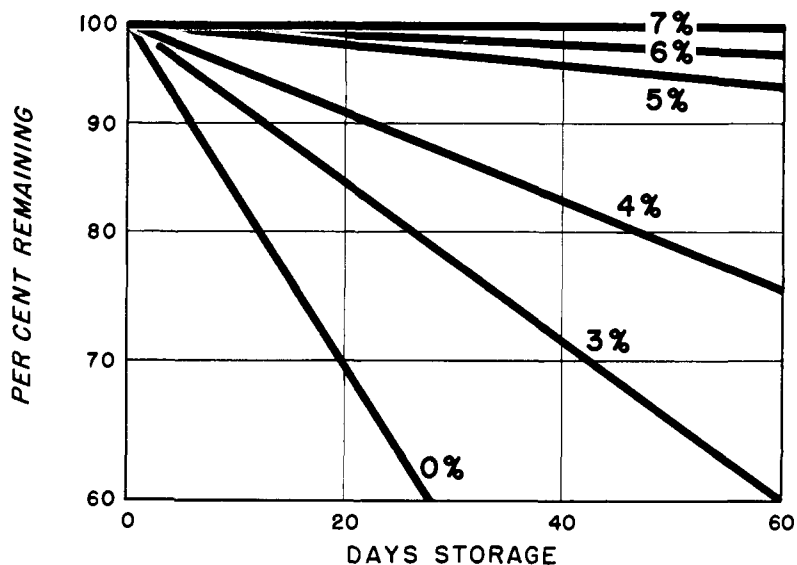


Figure 6. Stability of heptachlor formulated on Attaclay deactivated with diethylene glycol

apparent, subsequent tests were carried out at 122° F.

**Heptachlor Concentration.** It is evident from Table II that the rate of degradation is not proportional to heptachlor concentration. The absolute loss in concentration observed on storage is the same, irrespective of the initial concentration, while the percentage losses vary. This relationship is shown in Figures 4 and 5. The rates of change of concentration *vs.* time for three formulations of different concentration are equal, while the rates of change of the per cent of unreacted heptachlor decreases with increasing initial heptachlor content.

#### Deactivator Additives

Of all the materials screened for use as deactivators, oxygen-containing chemicals, as a class, showed the greatest effectiveness. Alcohols, ketones, glycols, and ethers all exhibited some degree of deactivating property. Stability data on some heptachlor formulations tested using oxygen-containing additives are shown in Table III. Alkaline materials such as caustic soda, hexamethylenetetramine, urea, lime, sodium carbonate, and calcium carbonate were not as effective as the oxygen-containing chemicals.

Many of the additives which perform satisfactorily as deactivators with the conditions of these experiments may prove to be less useful commercially than others. In some applications relative costs may be critical. In other instances the contribution of certain physical properties may be undesirable. Volatility of the additive is an important factor. Water or acetone, both of which deactivate carriers satisfactorily when their formulations are stored in sealed glass vessels, would probably not prove successful ordinarily because of their rapid escape. Flammability is another manufacturing consideration in the choice of deactivators. The selection of a deactivator for commercial application would depend on the evaluation of such factors.

The glycols were intensively investigated. This study revealed that either diethylene or triethylene glycol, at the same concentration, gives greater deactivation than monoethylene glycol. Diethylene glycol was chosen for a more detailed study.

**Diethylene Glycol.** Formulations were prepared and tested using increasing percentages of deactivator to determine the minimum effective concentration of diethylene glycol required with the various commonly used mineral carriers. Data obtained on carriers tested are given in Table IV and Figure 6. As increasing percentages of deactivator are used, the surface acidity decreases.

**Table II. Loss in Heptachlor Concentration during Storage of Various Concentrate Formulations**

Mineral Carrier	Initial Heptachlor Concentration, %	Loss in Concentration during Storage at 122° F. in Sealed Glass Jars					
		Absolute, %			% of Initial		
		10 days	30 days	60 days	10 days	30 days	60 days
Attaclay	25	...	6	8	16	24	32
	25	...	4	6	...	16	24
	25	...	5	7	...	20	28
	10	...	5	6	40	50	60
	10	...	5 1/2	7	...	55	70
	10	...	6	...	40	60	...
	2 1/2	All	...	...	100	...	...
Celite 209	25	1	3	4	4	12	16
	25	...	3	4	...	12	16
	10	...	2	4 1/2	...	20	45
	10	3/4	1 1/2	3 1/2	8	15	35
	9	3/4	2	4	8	22	44
	5	1	2 1/2	4	20	50	80

**Table III. Stability of 10% Heptachlor Formulations with Various Oxygen-Containing Additives at 122° F.**

Additive	Additive, %	Mineral Carrier	Heptachlor Assays (% of Initial Assay)	
			30 days' storage in sealed glass jars	60 days' storage in sealed glass jars
None		Attaclay	50	35
Acetone <sup>a</sup>	15	Attaclay	95	80
Acetone <sup>a</sup>	5	Attaclay	73	...
Tween 20, Atlas Powder Co.	5	Attaclay	100	100
Triton X-100, Rohm and Haas Co.	5	Attaclay	94	88
Emcol H85A, Emulsol Corp.	5	Attaclay	90	75
Isopropyl alcohol <sup>a</sup>	10	Attaclay	90	90
Diacetone alcohol	10	Attaclay	100	100
Ethylene glycol	7	Attaclay	93	84
Diethylene glycol	7	Attaclay	100	100
Triethylene glycol	7	Attaclay	100	100
None		Barden clay	11	1
Acetone <sup>a</sup>	10	Barden clay	100	100
Maracarb N, Marathon Corp.	6	Barden clay	100	100
Tween 20, Atlas Powder Co.	3	Barden clay	100	100
Water <sup>a</sup>	6	Barden clay	94	89
Triton X-100, Rohm and Haas Co.	3	Barden clay	100	100
Ethylene glycol	3	Barden clay	100	100
Diethylene glycol	3	Barden clay	100	100
Triethylene glycol	3	Barden clay	100	100

<sup>a</sup> Nonpermanent deactor due to volatility.

**Table IV. Stability of 10% Heptachlor Formulations with Mineral Carriers Deactivated with Diethylene Glycol**

Carrier	Diethylene Glycol, %	pKa of Formulation	Heptachlor Assays, % of Initial Assay	
			30 days at 122° F.	60 days at 122° F.
Attaclay	0	<1	50	35
	3	<1	84	60
	5	1	98	94
	6	>1	100	96
	7	3.3	100	100
	8	>3.3	100	100
arden clay	0	<1	11	1
	1	<1	100	92
	2	1	100	100
	3	3.3	100	100
Celite 209	0	<1	70	56
	1	1	100	100
	2	>1	100	100
	3	3.3	100	100

It appears that the threshold pKa value for stable heptachlor dusts is between 1 and 3. Using this technique, the proper percentage of diethylene glycol necessary with commonly used minerals was determined (Table V).

Equal effectiveness was observed when the deactivator was added prior to and simultaneously with the heptachlor, providing impregnation was uniform. Heptachlor and diethylene glycol, which are immiscible, can be simultaneously impregnated onto the carrier from one tank by mixing with a cosolvent such as isopropyl alcohol.

**Compatibility of Deactivated Heptachlor Formulations with Other Agricultural Chemicals**

Because heptachlor is often formulated with other agricultural chemicals, it was desirable to test the compatibility of the deactivated formulations with these materials. Some of the chemicals tested

**Table V. Diethylene Glycol Required to Deactivate Carriers for Use in Heptachlor Formulations**

Product	Manufacturers	%
Attaclay	Minerals and Chemical Corp., Philadelphia, Pa.	5-7
Dilux	Floridin Co., Warren, Pa.	5-7
Celite 209	Johns-Manville, New York, N. Y.	1-3
Celite 400	Johns-Manville, New York, N. Y.	1-3
Barden clay	J. M. Huber Corp., New York, N. Y.	2-3
Natka clay	National Kaolin, Aiken, S. C.	2-3
Vol dust	Valley Brick and Tile Co., Mission, Tex.	2-3
Rev dust	Milwhite Co., Houston, Tex.	6
Frianite	California Industrial Minerals Corp., Friant, Calif.	3
Vermiculite	Zonolite Co., Chicago, Ill.	1-3
Pioneer air float clay	Georgia Kaolin Corp., Elizabeth, N. J.	2-3
CCC diluent	Calcium Carbonate Co., Quincy, Ill.	0
Glendon pyrophyllite	Glendon Pyrophyllite Co., Greenboro, N. C.	0
Pyrax ABB	R. T. Vanderbilt, New York, N. Y.	0
Emtco	Eastern Magnesia Talc Co., Burlington, Vt.	0
Mil slip talc	Milwhite Co., Houston, Tex.	0
Panacalite	Combined Metals Reduction Co., Salt Lake City, Utah	0

were DDT, malathion, and parathion. In every case neither the chemical tested, the deactivator, nor the heptachlor was affected.

### Discussion

In 1955, deactivated mineral carriers were used in heptachlor formulations with excellent results. When the de-

activator is used in the correct amount and applied properly, heptachlor formulations with excellent storage stability can be prepared. Additional time and labor required in formulation are practically negligible, and the cost of the deactivator is in the range of 0.1 cent per pound of finished formulation when diluents such as talcs and pyrophyllites are used.

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## MODE OF ACTION OF PESTICIDES

# Reversal of Fungitoxicity of Copper-8-Quinolinolate

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Antimicrobial activity of copper oxinate (copper-8-quinolinolate) is reversed in the presence of excess metal ions and excess oxine (8-quinolinol). By employing a simplified experimental system, clear-cut demonstrations of the reversal phenomenon have been demonstrated. The conversion of the 2 to 1 (moles of oxine to copper) chelate to the 1 to 1 chelate in the presence of excess copper ions has been indicated by partition of the chelates between oil and water. Results support the mechanism of Albert and coworkers that the 1 to 1 chelate is the toxic entity and that equilibrium and cell penetration relationships account for the reversals of antimicrobial action.

THE PRACTICAL APPLICATIONS of 8-quinolinol (oxine) and copper-8-quinolinolate (copper oxinate) in industry and agriculture were previously reviewed (6). The present report considers one interesting aspect of the activity of oxine and its chelates—namely, the “reversal” phenomenon. This describes the condition where the inhibition of microbiological activity produced by the toxic chemical is antagonized by other materials and the microbiological activity is restored.

In 1943, Zentnyer (27) introduced the concept that oxine might be antifungal by virtue of its ability to precipitate from solution traces of metals necessary for fungus growth. As evidence, he cited an experiment in which a fungus that requires zinc in its metabolism was first poisoned by adding oxine to its growth medium and then restored to active growth by the further addition of a zinc salt (22).

Other workers reported reversal of

oxine toxicity with additional metals (Table I). Gale (7) distinguished between the reversal of the assimilatory and fermentation processes of the micro-organism with different metals. The precipitation concept, however, was soon confronted with data (10, 11, 16, 18) showing that the chelates formed from the reaction of oxine with metals were themselves as toxic as, or even more strongly antimicrobial than oxine. Moreover, the toxicity of the metal chelates could be reversed with metal ions. Thus, some other explanation for these interesting reversals was required.

Rubbo, Albert, and Gibson (13) proposed the theory that copper and iron chelates of oxine cause the oxidation of vital cell constituents such as thiol groups, and that in the case of gram-positive bacteria the metal cobalt prevents this oxidation. According to Vicklund and coworkers (19) the reversal of inhibition of metal ions results from

the workings of the mass action law in balancing the dissociation equilibrium so as to reduce the concentration of oxine ions. The oxine ion, they maintained, was the functional portion of the chelate in exerting toxic effects. Manten, Klöpping, and van der Kerk (10) failed to get reversals except under certain conditions. They attributed reversal phenomena to a lowering of the toxicant solubility below the inhibitory threshold, owing to the formation of a metal chelate which has a lower solubility in the growth medium than the free oxine. Anderson and Swaby (5) failed to get reversals with cobalt, zinc, manganese, iron, or copper, and got only a partial reversal with molybdenum. Albert, Gibson, and Rubbo (2) proposed an explanation of reversals based upon the dissociation of the 2 to 1 chelate (made up of 2 moles of oxine to 1 mole of metal) to the 1 to 1 chelate (made up of equimolar concentrations of oxine and metal). The latter chelate, said to be produced