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DDT STABILIZED COMPOSITIONS

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2 Claims. (Cl. 167—30)

(Granted under Title 35, U. S. Code (1952), sec. 266)

A non-exclusive, irrevocable, royalty-free license in the invention herein described, for all governmental purposes, throughout the world, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

We hereby dedicate the invention herein described to the free use of the people in the territory of the United States to take effect on the granting of a patent to us.

This invention relates to the improvement in the storage of liquid pesticidal formulations and the inhibiting of the corrosion of metallic containers.

An object of this invention is to stabilize emulsifiable concentrates so that the components of the concentrates do not react with each other and with the container with a resultant decrease in effectiveness.

Another object of this invention is to inhibit the corrosion of the container and prevent the deterioration of the emulsifiable concentrate by adding a material that does not interfere with the proper emulsification of the concentrate or reduce the efficacy of the emulsion as an insecticide. Another object of this invention is to stabilize pesticidal emulsifiable concentrates and prevent corrosion of their containers.

Another object of this invention is to prevent the loss due to the corrosion of metals in contact with corrosive oils, such as certain synthetic products, petroleum fractions, coal tar fractions, and other products of similar nature derived from these.

Another object of this invention is to prevent the loss due to corrosion in industrial concerns where corrosive liquids are held in metal pipes, vats, and tanks, and an inhibitor is needed which is sparingly soluble or not soluble in the liquids.

In many commercial plants the corrosion problem when certain corrosive liquids run through metal pipes or are held in tanks is serious. Any organic liquid or mixture which is of an acid nature, or has an acidity due to hydrogen bonding will tend to corrode metals. The exact mechanism by which oily liquids and organic solvents attack metals is rather obscure and of a controversial nature. We have found samples of isophorone with a pH as low as 3.0 and an acidity which cannot be exhausted by violent water washings. Our invention will minimize, retard, and control the ensuing corrosion, and has the added advantages of being either not soluble or sparingly soluble in the liquids, of stable nature, unreactive towards the liquids, and easily washed out with water or eliminated from the liquids.

This invention is based on the surprising discovery that

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the addition of small amounts of certain metallic thiosulfates and polythionates to emulsifiable concentrate formulations of insecticidal materials will stabilize these concentrates so that the reaction between the components with deterioration and the ensuing corrosion is greatly retarded. We have found that in certain formulations of insecticidal emulsifiable concentrates the components will react with each other even in glass containers.

Sodium thiosulfate has been found to be an inhibitor of the deterioration of a formulation consisting of lindane—20%, isophorone—40%, an alkylated naphthalene mixture, in this case Velsicol AR-60—32.5%, and an emulsifier, in this case Triton X-100—7.5%. This particular formulation is hereinafter referred to as LIVT. Tests have been made at ordinary or natural temperatures and accelerated or elevated temperatures. The results of a series of insecticidal packages in accelerated storage at 49° C. are presented in Table 1.

Table 1.—Effect of various concentrations of inhibitor on the rate of decomposition of LIVT formulations stored in different types of containers at 49° C.

Container identification	Type of can	Percent Na ₂ S ₂ O ₃	Remarks ¹
a	Electrolytic tinplate	0.05	Severe corrosion, blackish, black sediment.
b	do	.05	Removed from oven after 104 days.
c	do	.1	Moderate to severe corrosion, black, black sediment.
d	do	.1	Removed from oven after 124 days.
e	do	.2	Moderate to severe corrosion, black, black sediment.
f	do	.2	Removed from oven after 128 days.
g	do	.2	Do.
h	do	.5	Very slightly darker in color.
i	do	1.0	Severe corrosion, darker, sediment.
j	do	1.0	Removed from oven after 95 days.
k	do	1.0	Removed from oven after 107 days.
l	do	1.0	Removed from oven after 96 days.
m	1.25-pound tinplate	1.0	No significant changes.
n	Terneplate	1.0	Slight precipitate on walls.
Check	Electrolytic tinplate	0	Removed from oven after 28 days.
	1.25-pound tinplate	0	Removed from oven after 48 days.
	Terneplate	0	Removed from oven after 63 days.

¹ When a can became severely corroded and leaked, and the formulation became black, acid, and contained sediment, it was removed from the test. All others were observed at the end of 19 weeks.

The LIVT formulation without inhibitor showed severe corrosion and decomposition in 1 to 2 months in all types of containers, whereas all the samples with inhibitor were in satisfactory condition after approximately 5 months of accelerated storage.

The results of tests of the same nature at normal or natural temperatures (maximum 36° C., low 5° C., mean 26° C.) with different quantities of sodium thiosulfate in LIVT are shown in Table 2.

Table 2.—Effect of various concentrations of inhibitor on the decomposition of LIVT formulations in different types of containers after 4 months' storage at room temperature

ELECTROLYTIC TINPLATE						
Container designation	Percent Na ₂ S ₂ O ₃	Internal corrosion	Crystallization	Color	Chemical analysis	
					Inorganic Cl ¹	Percent lindane
o.....	1	None.....	None.....	O. K.....	None.....	20.5
p.....	0.05	do.....	do.....	O. K.....
g.....	.1	Slight.....	do.....	O. K.....
r.....	.2	V. slight.....	do.....	O. K.....
s.....	.5	None.....	do.....	O. K.....
Check.....	0	Severe.....	Heavy.....	Dark red..	5.0.....	14.5
1.25-POUND TINPLATE						
t.....	1	None.....	None.....	O. K.....
z ²	1	do.....	do.....	O. K.....	None.....	20.2
Check.....	0	Severe.....	do.....	Darker.....	do.....	18.9
TERNEPLATE						
v.....	1	None.....	None.....	O. K.....
Check.....	0	Slight.....	do.....	O. K.....
STANDARD						
.....	0

¹ Milligrams of inorganic chloride per 0.342-gram sample.

² Accelerated storage.

At the end of 4 months in normal storage there were no significant differences in the samples in various containers with different amounts of inhibitor, but as in the accelerated storage test, all of those with the inhibitor were superior to the check samples. The check samples in all types of containers showed from slight to severe corrosion of the cans, and the chemical analysis and biological tests on the formulation corroborated this visual estimation of decomposition. The formulations with inhibitor in electrolytic tinplate in normal and in 1.25-pound dipped tinplate in accelerated storage were equal to a freshly prepared standard in both the analytical and toxicity tests against mosquito larvae and flies.

In Table 3 are shown the results of 7 months' continuous storage at room temperature.

Table 3.—Effect of various concentrations of inhibitor on the decomposition of LIVT formulations in different types of containers after 7 months' storage at room temperature

ELECTROLYTIC TINPLATE				
Container designation	Percent Na ₂ S ₂ O ₃	Internal corrosion	Crystallization	Color
o.....	1	None.....	None.....	Slightly darker.
p.....	0.05	do.....	do.....	O. K.
g.....	.1	Slight.....	do.....	O. K.
r.....	.2	Very slight.....	do.....	O. K.
s.....	.5	None.....	do.....	O. K.
Check.....	.0	Severe—leaked ¹	Heavy.....	Reddish-black.
1.25-POUND TINPLATE				
t.....	1.0	None.....	None.....	O. K.
Check.....	.0	Severe.....	do.....	Darker.
TERNEPLATE				
v.....	1.0	None.....	None.....	O. K.
Check.....	.0	Slight general.....	do.....	O. K.

¹ Eliminated from the test at 5 months.

The same samples after 9 months in normal storage showed only slight or no corrosion of containers, no visible sediment, and a normal color. The check samples in the three types of containers showed for the terneplate slight general corrosion, for the 1.25-pound dipped tinplate severe corrosion, and for the 0.5-pound electrolytic tinplate elimination because of leaking at the end of 4 months of normal storage. From the experimental evidence in the check samples it is evident that the inhibitor is offering satisfactory protection under normal temperature conditions.

Anhydrous sodium thiosulfate has shown slightly better value as an inhibitor at ordinary temperatures while sodium thiosulfate pentahydrate has given better protection at elevated temperatures.

In carrying into practice this invention the finely divided thiosulfate salt is added freely or in a porous retainer in the calculate quantity to the emulsifiable concentrate immediately after it has been placed in the container in which it is to be stored. The container is closed tightly and the contents mixed well by shaking.

A DDT 1,1,1-trichloro-2,2-bis-(p-chlorophenyl) ethane formulation composed of DDT—25%, alkylated naphthalene—65%, and an emulsifier is also protected against deterioration in storage by the addition of sodium thiosulfate.

Although the examples given herein have contained sodium thiosulfates as the inhibitor, other water soluble thiosulfates and polythionates, such as ammonium and potassium may be used. The sodium, potassium, and ammonium salts of inorganic polysulfur acids of varying oxygen content, such as thiosulfates and polythionates, possess no toxicity in themselves, and do not interfere with the proper emulsification of the concentrate in the quantities used. They are water soluble and will not clog the spray nozzles when used in the spray.

It has been observed that the addition of water soluble thiosulfates, viz., sodium thiosulfate, inhibit the decomposition and corrosion of the container in the case of formulations containing other chlorinated hydrocarbon pesticides.

The thiosulfate salts protect the stability of the pesti-

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cidal formulation in glass and metal containers. These thiosulfate salts also inhibit the corrosion of metallic containers, thus insuring a decrease in loss of the contents through leakage.

The thiosulfate salts may also be used to inhibit corrosion in industrial installations of pipes and tanks, where normally corrosion will occur. The optimum amount of the inhibitor to add depends on the specific conditions under which it is used, such as flow rate through pipes, size of vats or tanks, and time the liquids are going to be kept in the vats or tanks. In tin-coated containers we have been able to stop corrosion by acid organic solvents for 3 to 5 months when the inhibitor sodium thiosulfate was used in concentrations of 1% to 0.1% under accelerated storage temperature of 120° F. Under normal room temperature conditions corrosion has been stopped for 9 months at least. The research does indicate that for shorter periods of time of storage or contact between corrosive liquids and metal, concentrations of 0.01% to 0.001% or lower may suffice. The in-

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hibitor may be added freely or in porous bags and any part remaining in the liquid, if necessary, may be eliminated by scrubbing with water and a phase separation.

It is to be understood that the above examples used in describing the use of these stabilizers and inhibitors are given only as examples and that this invention is not to be restricted by such use.

We claim:

1. A composition of matter comprising DDT—20—30%, alkylated naphthalenes—60—70%, emulsifier—3—10%, and sodium thiosulfate—0.1—2.0%.

2. An emulsifiable pesticidal concentrate comprising DDT, alkylated naphthalenes, an emulsifier, and an amount of sodium thiosulfate sufficient to prevent the interaction of the components of the concentrate and to prevent corrosion of metallic containers holding the same.

No references cited.