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Mast

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[54] **PESTICIDAL CONCENTRATES**

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[51] **Int. Cl.**..... **A01n 9/30;** A01n 9/32; A01n 9/36

[58] **Field of Search**..... 424/200, 352

[56] **References Cited**

UNITED STATES PATENTS

2,872,368	2/1959	Sanders et al.	424/352
3,683,078	8/1972	Haus	424/352

OTHER PUBLICATIONS

"Pesticides" – Neumeyer et al., – Chem. Week – April 11 and 26, 1969, pp. 6, 45, 61, 59 and 44.

McCutcheon's–Detergents & Emulsifiers – 1971 annual, Allured Publ. Corp., pp. 7, 9, 16, 27, 46, 66, 74, 104–105, 121 and 184–185.

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[57] **ABSTRACT**

Concentrated liquid pesticidal compositions comprising well defined amounts of certain sparingly water-soluble pesticides, certain nonionic surfactants, and certain phase modifying co-surfactants.

2 Claims, No Drawings

PESTICIDAL CONCENTRATES

BACKGROUND OF THE INVENTION

This invention relates to improved concentrated pesticidal compositions, which, when diluted in an aqueous medium, form clear stable homogeneous pesticidal emulsions.

Current needs for inherently safer pesticides which degrade rapidly into non-toxic substances once their purpose is accomplished, or alternatively may be utilized at lower levels, have focused interest on the use of pesticidal emulsions. In order to facilitate the preparation of emulsions, many pesticides are marketed in the form of emulsifiable concentrates typically comprising a pesticide, and an emulsifier (surfactant).

Typical concentrates when diluted have a characteristic milky or cloudy appearance because the droplets of the discontinuous (oil) phase are normally of the order of 1 to 25 microns in diameter. Due to the relatively large droplet size in such emulsions, there is a tendency for the organic material to coalesce upon standing to form separate layers.

In contrast, it has been discovered that liquid pesticidal concentrates containing certain nonionic surfactants and certain phase modifying co-surfactants can be prepared which, when diluted by water, will form optically clear homogeneous stable pesticidal emulsions. Apparently, the concentrates described herein form such emulsions due to the solubilization of the normally sparingly soluble pesticide in micellar structures. A micellar structure can be described as a colloidal aggregation of molecules, each molecule being generally characterized by a polar "head" and a hydrocarbon "tail." When in an aqueous media, the hydrocarbon portions of each molecule uniformly associate at the interior of the structure, and the polar portions at the exterior. The concentrates described herein, when diluted, are thought to form micelles on the order of 10^{-1} to 10^{-3} microns. Since the pesticide is solubilized in the micellar structures, there is no tendency for the organic phase to coalesce and the resulting emulsions remain stable and clear.

The use of nonionic surfactants in conjunction with co-surfactants in the preparation of toxic concentrates is known in the art. For example, U.S. Pat. No. 2,872,368 discloses toxic concentrates containing a nonionic derivative of polyglycol in combination with an oil soluble alkaline earth metal salt of an alkylated naphthalene sulfonic acid; and U.S. Pat. No. 3,683,078 discloses toxic concentrates containing a polyoxyalkylene derivation of an alkyl phenol, a sulfonate salt, and a polyoxyalkylene derivative of an alkanol.

It is also known, however, that commercially available pesticidal concentrates, including those containing nonionic surfactants, while forming clear emulsions when diluted, suffer several shortcomings. For example, many form stable emulsions at only certain levels of dilution or with only certain pesticides; and many cannot be applied using conventional spraying apparatus due to excessive foaming by the surfactant.

In contrast, it has been discovered that liquid pesticidal concentrates can be prepared which will solubilize certain normally sparingly water-soluble pesticides over a wide range of concentrations, which require significantly lower quantities of pesticide than previously known comparable systems, and which, when diluted by water, will form low foaming clear stable emulsions.

Moreover, the instant surfactant systems surprisingly enhance the wetting and spreading properties of pesticidal emulsions, thus providing for more efficient use of pesticide.

Accordingly, it is the principle object of the present invention to provide low cost liquid pesticidal concentrates which can be readily diluted to form clear homogeneous stable emulsions.

SUMMARY OF THE INVENTION

The present invention encompasses liquid pesticidal concentrates which may be readily diluted over a wide range of concentrations to form improved pesticidal emulsions, comprising (1) a sparingly water-soluble organic pesticide or mixture of pesticides; (2) a nonionic surfactant having a hydrophilic to lipophilic balance (HLB) of from 14 to 17; and (3) a phase modifying co-surfactant.

DETAILED DESCRIPTION OF THE INVENTION

Objects of the present invention are achieved by providing liquid, pesticidal concentrates. The first essential ingredient of said concentrates is from about 5 to about 40 percent, preferably from about 15 to about 25 percent, by weight of a sparingly water-soluble organic pesticide selected from the group consisting of allethrin, diazinon, malathion, ronnel, toxaphene, diallate, bis(tri-hexyl tin)oxide, phenylsulfonylmethyltri-hexyl tin, phenylsulfonylmethyl-tri-butyl tin, propanil, the octyl ester of 2,4-dichlorophenoxyacetic acid, and the butyl ester of 2,4-dichlorophenoxyacetic acid.

As used herein, the term "sparingly water-soluble" means having a solubility in water of less than about 0.1 percent by weight at 25°C.

The pesticides suitable for use in the present invention although primarily herbicides and insecticides (acaricides and miticides) also include fungicides, bactericides and the like. Suitable pesticides may be either in liquid or solid form and may be selected from a wide range of chemical structures. Pesticides in a liquid state can be directly incorporated into the concentrate compositions. Such liquid pesticides can be typically incorporated up to about 15 percent by weight. Pesticides in a solid state can be incorporated into the concentrate compositions by initially dissolving the pesticide in a suitable solvent such as N-methylpyrrolidone, methyl ethyl ketone, dimethyl formamide, and the like and subsequently treating the resulting solution as if it were the pesticide. Such solid pesticides can typically be incorporated up to about 10 percent by weight. Solid pesticides which do not dissolve to at least 25 percent in common solvents cannot be incorporated into the present systems.

Many organic, sparingly water-soluble insecticides are suitable for use in the concentrates herein. Some typical examples are the following.

1. Sparingly water-soluble chlorinated hydrocarbon insecticides such as toxaphene.
2. Sparingly water-soluble organophosphorous insecticides such as diazinon, malathion, and ronnel.
3. Sparingly water-soluble pyrethroid-like insecticides such as allethrin.

Preferred insecticides for use herein include toxaphene, diazinon, malathion, ronnel, allethrin, and mixtures thereof. These insecticides show unexpected and significant enhancement in insecticidal activity which

is obtained when these insecticides are applied in clear emulsion form.

Many organic, sparingly water-soluble herbicides are suitable for use in the concentrates herein. Some typical examples are the following:

1. Sparingly water-soluble chlorophenoxy herbicides such as 2,4-dichlorophenoxyacetic acid and its herbicidally active esters.
2. Sparingly water-soluble thiocarbamate herbicides, such as diallate.
3. Sparingly water-soluble chlorinated anilide herbicides such as propanil.

Certain organic sparingly water-soluble herbicides are preferred for use in the concentrates herein because of the unexpected and important enhancement in herbicidal activity which is obtained for these herbicides when applied in the clear emulsion form. The preferred herbicides include the octyl and butyl esters of 2,4-dichlorophenoxyacetic acid, diallate, propanil, and mixtures thereof.

In addition to the above insecticides and herbicides, organic sparingly water-soluble organotin compounds are suitable for use herein. These compounds, are primarily useful as acaricides, fungicides, bactericides, algicides, or molluscicide. Some typical examples of suitable organotin compounds include bis(tri-hexyl tin)oxide, phenylsulfonylmethyltri-hexyl tin, phenylsulfonylmethyl tri-butyl tin, and mixtures thereof.

The second essential ingredient of the instant concentrates is from about 20 to about 65 percent, preferably from about 30 to about 50 percent, by weight of a liquid nonionic surfactant having a hydrophilic to lipophilic balance (HLB) of from 14 to 17.

According to the HLB system, surfactants are classified by the size and strength of the hydrophilic and lipophilic portions of the molecule. The balance in the size and strength of these two opposing groups is called hydrophile-lipophile balance or HLB. An emulsifier that is lipophilic in character is assigned a low HLB number, while an emulsifier that is hydrophilic in character is assigned a high number. The values that have been assigned to emulsifiers range from one to forty. The midpoint is about ten. A thorough explanation of hydrophilic-lipophilic balance can be found in Osipow, L.I. Surface Chemistry (1962), incorporated herein by reference.

A wide variety of nonionic surfactants are known to the art and are suitable for use herein. Typical examples of suitable nonionic surfactants are:

a. Compounds having an HLB number from 14–17 derived from the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms (preferably about 10 to 18), in either straight chain or branched chain configuration, with from about 3 to 30 moles of ethylene oxide.

b. Compounds having an HLB number from 14–17 derived from the condensation product of alkyl- or dialkyl-phenols, having from about 8 to 15 carbon atoms in the alkyl chains, with from about 3 to about 30 moles of ethylene oxide.

c. The fatty acid esters of polyoxyethylene sorbitan having an HLB number from 14–17.

d. Compounds having an HLB number from 14 to 17 derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine.

Many other nonionic surfactants are known in the art and are suitable for use herein. (See McCutcheon's Detergents and Emulsifiers, 1971 Ed., Allured Pub. Co., Ridgewood, N.J., incorporated by reference herein.). Further examples of suitable surfactants also appear in the working examples herein. The preferred nonionic surfactants for use herein are oleyl sorbitan ester condensed with about 20 ethoxylate groups, lauryl sorbitan ester condensed with about 20 ethoxylate groups, lauryl sorbitan ester condensed with about 20 ethoxylates, myristyl sorbitan ester condensed with about 20 ethoxylates, oleyl alcohol condensed with about 20 ethoxylates, and nonylphenol condensed with about 20 ethoxylates.

The third and final essential ingredient of the instant concentrates is from about 20 to about 65 percent, preferably from about 30 to about 50 percent, by weight of a phase modifying co-surfactant selected from the group consisting of the C_6–C_{10} alkyl diethanol amides, the condensation product of 1 mole of decyl alcohol with an average of about 6 moles of ethylene oxide, and the condensation product of 1 mole of oleyl alcohol with an average of about 10 moles of ethylene oxide.

Phase modifying co-surfactants are defined herein as surfactants which promote the solubilization of organic materials, such as the organic sparingly water-soluble pesticides herein, in water plus emulsifier systems, i.e., the co-surfactants herein promote the formation of a single phase emulsion when the instant concentrates are diluted by an aqueous media. Although similar to the emulsifiers disclosed above, in that both groups possess surface active properties, the phase modifying co-surfactants presently detailed have the unique ability to promote solubilization of the above pesticides in combination with nonionic surfactants having an HLB of 14 to 17. Thus, for purposes of this invention, a distinction must be made between the primary nonionic emulsifiers and the phase modifying co-surfactants.

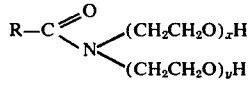
Organic, sparingly water-soluble pesticides can be formulated into liquid pesticidal concentrates by thoroughly mixing them with a nonionic surfactant having an HLB of 14–17 (emulsifier) and a phase modifying co-surfactant. If the pesticide is a solid at room temperature, it may be necessary to dissolve the pesticide in a suitable organic solvent. In order to obtain the concentrates, it is essential that the pesticide, emulsifier, co-surfactant, and solvent (if necessary) be present in certain proportions. As described hereinafter, other ingredients can be included in these compositions if desired.

Due to the fact that the pesticides suitable for use herein are of differing chemical and physical types, the proportion of components suitable for achieving a concentrate of one pesticide may not be the same as for another. No steadfast rules are known whereby prediction of the precise pesticides this system will solubilize or the precise proportions needed can be made. Likewise, the same surfactant pair which is suitable for formulating concentrates of one pesticide may not be suitable for another. Some empirical testing may be required, therefore, in order to select a suitable surfactant pair and the necessary proportions of components for obtaining a liquid concentrate of a particular pesticide. Such empirical testing is well within the skill of those engaged in the emulsion art.

As noted previously, a special circumstance arises when the pesticide does not dissolve in the surfactant system. This can occur particularly in the case of many solid pesticides. In such cases, one may choose an additional solvent and proceed by first dissolving the pesticide in an organic solvent (e.g., N-methylpyrrolidone, methyl ethyl ketone, dimethyl formamide, dimethyl sulfoxide, etc.) and subsequently treating the resulting solution as if it were the pesticide. Pesticides which do not form at least a 25 percent solution in such solvents cannot be incorporated into the concentrates disclosed herein.

The pesticidal concentrates herein are most easily formulated when starting with pure, or at least "technical grade" pesticide since this reduces the number of extraneous (and in most cases unknown) materials which are introduced into the formulation and which can adversely affect the ease with which a concentrate can be attained. Therefore, the use of pesticides having a purity of at least "technical grade" is preferred herein.

The concentrates herein can contain combinations of organic, sparingly water-soluble pesticides. Likewise, the concentrates may contain additional materials. For example, lipophilic surfactants (usually liquid) can be used to replace part of the original surfactant/co-surfactant pair in amounts of from about 5 to 20 percent by weight. Such materials often cause a further enhancement of pesticidal efficacy. Various non-limiting examples of suitable adjuvant lipophilic surfactants include compounds of the formula



wherein R is alkylaryl or straight or branched chain alkyl containing from about 8 to 18 carbon atoms and x and y are integers having a sum of from about 1 to 8; compounds of the formula R-O $(CH_1CH_2O)_xH$ wherein R is as defined above and X is an integer from about 2 to 8; and fatty alcohols containing from about 8 to 14 carbon atoms.

Incorporation of such adjuvant surfactants necessarily involves replacement of part of one or more of the essential ingredients (i.e., pesticide, nonionic, or co-surfactant) of the concentrates herein, and may in some cases require modification in the basic concentrate formula so as to maintain the desirable character. In other words, an established composition for a given pesticide may have to be modified if other pesticides or additives are incorporated.

The following examples are given by way of illustration and are in no way to be construed as limitations on the invention claimed herein.

Table I below sets forth a wide variety of liquid pesticides and acaricides which have been employed in the concentrate compositions described above. The concentrates were prepared by adding the neceesary quantity of pesticide to a solution of equal parts of oleyl sorbitan ester condensed with 20 ethoxylate groups (Tween 80 supplied by Atlas Chemical Ind.) and decyl diethanol amide, and mixing thoroughly.

TABLE I

ETHOXYLATED OLEYL SORBITAN ESTER-DECYL DIETHANOL AMIDE SYSTEMS

Ex.	Pesticide	Type	Concentrate Ingredients, % by Weight			
			Pesticide	Nonionic	Cosurfactant	Other*
I	Allethrin	Insecticide	15.0	42.5	42.5	—
II	Diazinon	Insecticide	38.7	27.7	27.8	5.8
III	Malathion	Insecticide	9.8	45.1	45.1	—
IV	Diallate	Herbicide	14.8	41.8	41.7	1.7
V	Octyl ester of 2,4-D	Herbicide	14.9	42.6	42.5	—
VI	Butyl ester of 2,4-D	Herbicide	15.1	42.5	42.4	—
VII	Bis(tri-hexyl tin)oxide	miticide	14.8	42.6	42.6	—
VIII	Phenylsulfonylmethyltri-hexyl tin	Acaricide	15.1	42.5	42.4	—
IX	Phenylsulfonylmethyltri-butyl tin	miticide	14.9	42.6	42.5	—

*In all examples, "Other" refers to impurities in the pesticides or solvents.

The foregoing compositions are diluted with water to provide clear, homogeneous, stable emulsions having a concentration of pesticide of from about 0.01 to 2.5 percent by weight. These emulsions provide a high level of pesticidal activity.

Equivalent amounts of the following nonionics having an HLB of 14–17 are substituted in the above compositions for the ethoxylated oleyl sorbitan ester: lauryl sorbitan ester condensed with 20 ethoxylate groups, myristyl sorbitan ester condensed with 20 ethoxylate groups, and nonylphenol condensed with 20 ethoxylate groups, with comparable results.

Equivalent amounts of the following co-surfactants are substituted in the above compositions for the decyl diethanol amide: decyl alcohol condensed with 6 ethoxylate groups and oleyl alcohol condensed with 10 ethoxylate groups with comparable results.

Table II below sets forth the use of a solvent to dissolve solid pesticides prior to incorporation into the ethoxylated oleyl sorbitan ester-decyl diethanol amide solution to form concentrates. These systems were prepared by dissolving the necessary quantity of pesticide in N-methyl pyrrolidone (NMP), then mixing this solution thoroughly with the required amount of solution. Upon dilution with water to use concentrations (0.01 – 2.5 percent), clear, micellar physically stable emulsions are formed.

TABLE II

ETHOXYLATED OLEYL SORBITAN ESTER-DECYL DIETHANOL AMIDE SOLVENT SYSTEMS

Ex.	Pesticide	Type	Concentrate Ingredients, % by Weight				
			Pesticide	NMP	Nonionic	Co-Surfactant	Other
X	Ronnel	insecticide	10.0	15.1	37.5	37.4	—
XI	Toxaphene	insecticide	10.1	15.2*	37.4	37.3	—
XII	Propanil	herbicide	9.8	15.3	37.4	37.5	—

*Solvent — methyl ethyl ketone

The foregoing compositions are diluted with water to provide clear, homogeneous, stable emulsions having a concentration of pesticide of from about 0.01 to 2.5 percent by weight. These emulsions provide a high level of insecticidal activity against a wide variety of insect species.

Equivalent amounts of the following solvents are substituted in the above compositions for NMP: dimethylformamide, dimethyl acetamide, dimethyl sulfoxide, acetone, and methyl ethyl ketone, with comparable results.

The following example is intended to illustrate a concentrate system which was formed from a mixture of pesticides incorporated into a nonionic plus co-surfactant system. The concentrate was prepared by adding necessary quantities of pesticides to the solution, then mixing thoroughly. Since one of the pesticides was a solid, it was first dissolved in methyl ethyl ketone before mixing. Upon dilution with water to use concentrations (0.01 – 2.5 percent), a clear stable emulsion is formed, which shows a high level of pesticidal activity.

EXAMPLE XIII

PESTICIDE MIXTURE

Components	Concentrate Composition by Weight %
Toxaphene	12.0
Diazinon	12.0
Oleyl sorbitan ester condensed with 20 ethoxylate groups	29.3
Decyl diethanol amide	27.4
Methyl ethyl ketone	17.6
Other	1.7

In the foregoing composition, 10 percent of the original surfactant/co-surfactant pair is replaced by the lipophilic condensation product of octylphenol with an average of 6 moles of ethylene oxide. Upon dilution to use level, a clear stable emulsion is formed, which shows an enhanced level of pesticidal activity.

The pesticidal concentrates described herein are conveniently applied in dilute emulsion form to insects, or to plants, in the form of a spray, foam or aerosol just as in the case of conventional concentrates. Other means such as immersion, drenching, etc. can also be used if desired. Accordingly, the present development also encompasses methods for using the pesticidal concentrates, hereinabove, by diluting the concentrates to use level emulsions; and contacting the pest to be controlled with a safe and effective amount of said emulsion.

The term "contacting" is intended to include direct application to the pest as well as application to habitat or vicinity. Thus, in the case of herbicidal emulsions, contact includes, for example, contacting the plant itself as well as the soil; and in the case of insecticidal emulsions, contact includes, for example, contacting the pest, its habitat, or its food.

Although the pesticidal concentrates discussed above can be readily diluted over a wide range of concentrations dependent primarily upon the nature of the pesticide, the degree of infestation, and the choice of the user, it has been determined that for maximum efficacy use level dilution is normally from about 0.01 to about 2.5 percent by weight pesticide (Unless indicated otherwise, use level concentrations are in percentage by weight of pesticide per total use level weight of the emulsions.) When applied broadcast, within these normal ranges of dilution, the emulsions which result from dilution are unusually effective at rates of from about ⅛ pound per acre to about 20 per acre. For insecticidal emulsions, the preferred rates of application, assuming normal dilution, are from about ⅛ pound per acre to about 10 pounds per acre. For herbicidal emulsions the preferred rates of application, again assuming normal dilution are from about 1 pound per acre to about 20 pounds per acre.

What is claimed is:

1. A concentrated liquid composition comprising From about 1 to 40 percent, by weight, of diazinon, and the balance, equal parts, by weight, of

1. ethoxylated oleyl sorbitan ester having a hydrophilic to lipophilic balance of 15, and

ii. decyldiethanol amide.

2. The concentrated liquid of claim **1** comprising from 5 to 40 percent, by weight, diazinon.

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