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Liquid Formulations of 1-(3,4-Dichlorophenyl)-3-methoxy-3-methylures and 2-Chloro-N-isopropylacetanilide

Abstract of the Disclosure

This invention relates to novel liquid formulations containing a mixture of 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea, 2-chloro-N-isopropylacetanilide in a suitable solvent. Such formulations can also contain an emulsifier and/or a co-solvent. The formulations of this invention are surprisingly stable when stored at low temperatures.

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Background of the Invention

This invention relates to novel liquid agricultural formulations stable at low temperature and useful as herbicides. The active component in the formulation is a mixture of 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea, hereinafter called linuron, and 2-chloro-N-isopropylacetanilide, hereinafter called propachlor.

Linuron and propachlor are herbicides that have each found wide application in weed control programs. It is also known that combinations of linuron and propachlor exhibit outstanding weed control in corn, sorghum and soybeans both in pre-emergence and post-emergence applications.

These herbicides have been prepared for use either as granules or as wettable powders. Because of the irritating and toxic nature of propachlor, the dustiness of dry formulations such as wettable powders represents not only an irritation, but also an actual hazard to persons carelessly handling these formulations. This hazard is of particular importance in the manufacture of wettable powders where the requirement of dust-tight equipment increases the cost and difficulty of producing the formulation. The properties of both linuron and propachlor are such that a solution concentrate of either ingredient is difficult to produce.

Agricultural weed killers, like many other formulated products, must meet a variety of exacting requirements before they are commercially useful. In the case of liquid formulations, they must be stable in storage. Concentrates for application in water must emulsify well when diluted at many different concentrations with water of different types and hardness.

It is known that solution concentrates of linuron or of propachlor, at economically practical concentrations, are not stable to cold temperature storage. Crystals of the active ingredient will form in said concentrates of linuron or of propachlor at even moderately low temperatures. When crystallization occurs in large containers as, for example, in a 30-gallon drum in a warehouse, such crystals form dense, thick layers at the bottom of the drum. It is usually impractical or at least very difficult to re-establish a homogeneous solution even when the contents of the drum are warmed. It was, therefore, believed that dry formulations such as wettable powders and granules, in spite of their hazards, were the most acceptable type of formulations for this combination of herbicides.

It has now been discovered that a formulation of linuron and propachlor when combined at a weight ratio of linuron to propachlor of from 1:1 to 1:3 and dissolved in a suitable solvent are surprisingly stable when stored at low temperatures. Formulations as hereinafter described have better low-temperature storage characteristics than either active constituent at the concentration of said constituent in the mixture with an especially surprising increase in linuron stability. It has, therefore, been discovered that combining linuron and propachlor in a liquid system results in a synergistic depression of the cloud point of the system and enhancement of the low-temperature storage characteristics. The term "low-temperature" will be understood to refer to temperatures in the range of 0° to 5° C. and lower. For practical purposes, a formulation which is stable at a temperature of from 0° to 5°C. will be sufficiently

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stable to withstand the coldest temperatures encountered under normal storage conditions.

The practice of this invention also results in lower manufacturing costs as the liquid formulations herein claimed can be prepared by dissolving the herbicidal components and agricultural modifiers in simple equipment, moreover dust contamination is not a hazard. In addition, the user of the formulation finds it easy to measure and pour the formulations of this invention with minimum skin exposure and no risk of breathing the dusts inherent in the handling of wettable powders.

Summary of the Invention

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This invention relates to novel liquid formulations containing linuron, propachlor, and a solvent such as an aromatic hydrocarbon or a halocarbon. The formulations of this invention will contain from 15-50% by weight active ingredient. The active ingredient consists of a combination of linuron and propachlor in which the linuron to propachlor weight ratio is from 1:1 to 1:3. The preferred formulations of this invention also include an emulsifying agent. In addition, the formulations of this invention can include a co-solvent and an oil-soluble corrosion inhibitor. Preferred co-solvents are alkylbenzenesulfonic acids such as dodecylbenzenesulfonic acid, nonylbenzenesulfonic acid and phenolic compounds such as phenol, the cresols and resorcinol. Such co-solvents can comprise up to 40% of the total solvent present in the formulation.

Detailed Description of the Invention

As indicated above, the active ingredient is a mixture of linuron and propachlor. The linuron component of

the formulations of this invention can be prepared by reacting N,0-dimethylhydroxylamine with 3,4-dichlorophenyl isocyanate as described in U.S. Patent No. 2,960,534. The propachlor component of the formulation of this invention can be prepared by reacting the acid chloride of α-haloacetic acid with N-isopropylaniline according to the method taught in U.S. Patent 2,683,752.

As discussed above, the active ingredient will be present in an amount of 15-50% by weight of the total weight of the composition with a concentration of from 25-45% by weight being preferred.

The 15% by weight lower limit is not critical for obtaining stable formulations, since a lesser amount of active in the formulation would be operable, but this limitation is set because less concentrated formulations would be uneconomic.

As the upper limit of 50% by weight is approached, the low-temperature stability of the composition becomes the limiting factor. In general, it is not possible to produce compositions containing more than 50% active ingredient and at the same time maintain freedom from crystal formation at the very low temperatures occasionally encountered in practical storage of agricultural chemicals.

The emulsifiable liquid formulations of this invention are preferred. They will contain from about 24 to 84% by weight halocarbon or aromatic hydrocarbon as the solvent. It will be understood that the term aromatic hydrocarbon solvent as used herein includes compounds such as alkylated benzenes, alkylated naphthalenes and the like; with the limitation that said solvents are within the distillation range of from about 132°-371°C., are comprised of greater than 80% aromatics and have a flash point above 26°C.

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Commercially available aromatic hydrocarbon solvents such as the following are suitable for use in preparing the formulations of this invention.

"Espesol"* #5 (Mfd. by Signal Oil and Gas Co.)

"Panasol"* AN-3 (a high-boiling naphtha Mfd. by Amoco Chemicals Corp.)

Harrett Industrial Xylol (Mfd. by Allied Chemical and Dye Corp.)

Sinclair Xylol (Mfd. by Sinclair Chemicals Inc.)

"Picco"* Hi Solv. 30 (Mfd. by Penn Industrial Chemicals Corp.)

"Velsicol"* Ar-60 (Mfd. by Velsicol Corp.)

"Velsicol"* AR-40 (Mfd. by Velsicol Corp.)

It will be understood that the term halocarbon solvent as used herein includes normally liquid, partially halogenated aromatic and aliphatic hydrocarbons.

Of the many aromatic halocarbon solvents available chlorobenzene, o-dichlorobenzene, trichlorobenzene and bromobenzene are preferred because of their economy and their low temperature solvency.

Of the many aliphatic halocarbon solvents available, those containing from one to three carbon atoms, at least one hydrogen atom and two or more halogen atoms per molecule are preferred. Particularly suitable for a balance of properties are chloroform; 1,1,2-trichloroethane; 1,1,2,2-tetrachloroethane; pentachloroethane and trichloroethylene.

It will also be understood that the solvent system can be a mixture comprised of one or more aromatic hydrocarbon solvents and one or more halocarbon solvents to achieve the balance of properties desired.

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^{*} denotes trade mark

In a liquid formulation intended for direct low-volume application, the solvent may have greater water-solubility than can be tolerated in an emulsifiable concentrate. Thus an additional group of solvents can be used for such a purpose. The solvents described above for emulsifiable concentrates are still practical and most preferred. Additional highly preferred solvents are N-methylpyrrolidone, benzaldehyde, "Cellosolve"*, and dimethylformamide. Other preferred solvents are:

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anisole

isoamyl alcohol

1,3-butylene glycol

ethylene glycol, methyl ether, acetate
diethylene glycol, butyl ether
diethylene glycol, butyl ether, acetate
cyclohexanone
acetophenone
isophorone

pentoxone

furfural

dimethylacetamide

tetramethylurea

nitroethane

nitrobenzene

bis(2-chloroethyl) ether

2-chloroethanol

In addition, many suitable solvents useful for preparing the formulations of this invention are listed in I. Mellan, Handbook of Solvents, Reinhold Publishing Company, 1957.

^{*} denotes trade mark

In addition to the solvent system, it is sometimes advantageous that up to 40% of the solvent be replaced with a co-solvent. The compounds suitable for incorporation as co-solvents are highly polar materials such as methanol, dimethylformamide, N-methyl-2-pyrrolidone, benzyl alcohol, benzaldehyde, furfural, alkylamines, nitrobenzene, phenolic compounds and alkylbenzenesulfonic acids.

Of the above-described co-solvents, the alkylbenzene-sulfonic acids and phenolic compounds are preferred.

Preferred formulations of this invention will include as a co-solvent from 5-25% by weight of alkylbenzenesulfonic acids such as dodecylbenzenesulfonic acid or nonylbenzenesulfonic acid in place of a corresponding amount of solvent.

Also preferred are formulations containing from 5 to 25% of phenolic co-solvent. Preferred phenolic co-solvents are mono- and dihydroxybenzenes optionally substituted with lower alkyl or halogen. Particularly preferred for low cost and high efficiency as co-solvents are phenol, the cresols, and resorcinol. The phenolic co-solvents need not be in a highly pure state. For example, a typical technical cresol containing 54% m-cresol, and 29% p-cresol also contains 17% other phenols which product is beneficial as a co-solvent.

In order to make the formulations of this invention useful in aqueous sprays for weed control on corn, sorghum and soybeans, the formulation must contain an emulsifying agent. In some instances, the alkylbenzenesulfonic acid co-solvent can function as the emulsifying agent. In the absence of, or in addition to, an alkylbenzenesulfonic acid co-solvent a conventional emulsifying agent can be present in an amount

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of 1-10% by weight of the formulation. Many suitable emulsifying agents are listed in McCutcheon's <u>Detergents</u> and <u>Emulsifiers Annual</u>, 1967. Anionic, cationic and nonionic emulsifiers can be used, but anionic and nonionic emulsifiers are preferred. Suitable emulsifying agents include:

Alkali metal, alkaline earth, and amine salts of alkylarylsulfonic acids.

Alkylphenoxy polyethoxy ethanols

Alkoxypolyethoxy ethanol phosphates

Alkylphenoxy polyethoxy ethanol phosphates

Polyoxyethylene amines

Polyethoxylated alkyl alcohols

Polyethyleneoxide adducts of fatty acids and rosin acids

Petroleum sulfonates

Polyethoxylated vegetable oil

Polyoxyethylene sorbitan fatty acid esters

Polyoxyethylene sorbitol fatty acid esters

Polyoxyethylene glycerol fatty acid esters

Polyoxyethylene adducts to long-chain mercaptans.

Mixtures of emulsifying agents such as the ones listed above are often used and are frequently preferred.

In addition, it may be desirable to include a small amount of an oil-soluble corrosion inhibitor in the formulations of this invention.

This discussion has concerned itself with a description of liquid herbicidal formulations of linuron and propachlor which are surprisingly stable at low temperatures.

It has also been discovered that mixtures of linuron with 2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide exhibit similar enhanced solubility. For example at a 1:1 ratio of

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actives in an aromatic naphtha: methanol system the cloud point of the mixture is surprisingly decreased well below the cloud point of linuron alone in the same system.

Iow-temperature stability limits can be measured by storing samples in a controlled temperature chest, seeding with tiny crystals of pure materials and observing the growth or disappearance of crystals after a period of several days. If no crystals form, the process is then repeated at a lower temperature, until the limit of stability has been found. However, low-temperature characteristics can be also meaningfully, rapidly and conveniently measured by a determination of the cloud point of the system.

A cloud point is the equilibrium temperature at which solids first separate from a previously clear solution. For example, if a solution has a cloud point of 5°C., then a solution which is cooled to 5° would be expected to have the first solids and be in equilibrium with saturated solution. In practice, to avoid supercooling effects, cloud points are usually measured by cooling a solution further, to obtain a copious crop of crystals. The solution is slowly warmed and the temperature at which the crystals finally disappear is determined. Using this technique, it has been found that solutions of propachlor or linuron singly have higher cloud points than the solutions of the combination.

Generally, the formulations of this invention will have a cloud point of 5°C. or lower with those formulations being preferred which have a cloud point below 0°C. It will, of course, be understood that the stability requirements for a particular formulation will be contingent on the time of year the formulation is shipped, length of storage planned, and geographic destination of the formulation. Usually a

cloud point of about 5°C. is acceptable although a formulation with a lower cloud point will be employed when the formulation is to be shipped or stored in cold climates during the winter season.

To further illustrate the low temperature stability of a linuron-propachlor-solvent system a cold storage test can be run. This type of test differs from the cloud point determination in that equilibrium conditions are attained in the cold storage system, while a dynamic aspect is present in a cloud point determination. The cold storage test for solution stability is run as follows:

Purified linuron, purified propachlor and commercial "Triclene"*, technical (trichloroethylene, technical) are used in the procedure. Samples containing various ratios and concentrations of linuron, propachlor and linuron-propachlor mixtures are placed in a cold chest. The temperature is lowered and samples are seeded with traces of dust of the active ingredients after the solution has been cooled to the test temperature of -5°C. The samples are then observed over the course of at least 3 to 4 days to determine whether crystallization has occurred. When the temperature of the system is maintained within the range of -4.5° to -5.0°C. for four days after seeding the following results are observed:

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TABLE I

Cold Storage Test at -5°C.

Actives Ratio		Active ntration	Max. Solu	bility Range
Propachlor:Linuron	Max. Stable	Min. Unstable	Linuron	Propachlor
1:0	18%	20%	-	18 - 20%
0:1	4%	5%	4-5%	-
1:1	1%	14%	6.5-7%	6.5-7%*
2:1	30%	31%	10-10.3%	20-20.7%
3:1	28%**	•	>7%	> 21%

*The propachlor ratio appears low because the selected ratio ties the propachlor concentration to the linuron concentration and therefore the propachlor concentration does not appear high when the formulation becomes unstable. However, even at a 1:1 ratio the combination results in a 30% increase in linuron solubility in the formulation while the above data further shows that the linuron content of the 3:1 solution can be increased 40% beyond what is possible in a system not containing propachlor.

^{**}Highest concentration of 3:1 formulation in test.

The compositions of this invention can be used to selectively control weeds in crops, particularly corn, sorghum and soybeans. The compositions can be applied at rates of 1 to six kilograms per hectare. The exact rate to be used will depend upon the crop, the soil type, the climate and the weeds to be controlled. The treatment will control both broadleaved weeds and grasses. The exact rate to be used can be readily selected by one skilled in the art from the available literature.

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The following Examples are presented to further illustrate this invention. Parts and percentages in the following Examples are by weight.

Example 1

An emulsifiable concentrate is prepared by stirring the ingredients listed below until solution is complete.

Linuron	10%
Propachlor	20%
Dodecylbenzenesulfonic acid	19%
"Panasol" AN-3	51%

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The cloud point of the emulsifiable concentrate of Example 1 is less than 0°C.

Three kilograms of the active ingredients formulated as described above are emulsified in 300 l. of water and applied pre-emergence to one hectare of corn planted in a Clarion silt loam soil. The treatment controls giant foxtail (Setaria faberii), crabgrass, velvetleaf, goosegrass (Eleusine indica), barnyardgrass, prostrate spurge (Euphorbia supina), Pennsylvania smartweed (Polygonum pensylvannicum), and the corn grows and produces a good yield.

Example 2

An emulsifiable concentrate is prepared by stirring the ingredients listed below until solution is complete.

Linuron	7.5%
Propachlor	7.5%
Nonylphenoxy polyethoxyethanol	5.0%
"Espesol" #5	80.0%

Two kilograms of active ingredient formulated as described are emulsified in 200 l. of water and applied pre-emergence to a hectare of soybeans planted in a silt loam soil. The treatment provides control of crabgrass (Digitaria spp.), flower-of-an-hour (Hibiscus trionum), velvetleaf (Abutilon theophrasti), barnyardgrass (Echinochloa crusgalli), the foxtails (Setaria spp.), pigweed (Amaranthus retroflexus), and witchgrass (Panicum capillare). The soybeans grow and produce a good yield, free of weed competition.

Example 3

An emulsifiable concentrate is prepared by stirring the ingredients listed below until solution is complete.

20	Linuron	7.5%
	Propachlor	22.5%
	O-cresol-cosolvent	15.0%
	Polyoxyethylene sorbitan fatty acid ester	5.0%
	"Velsicol" AR-40	50.0%

Four kilograms of active ingredients in the above formulation are emulsified in 250 l. of water and applied pre-emergence to a hectare of corn planted in a Muscatine silt loam. The treatment controls the foxtails, crabgrass, goosegrass, barnyardgrass, Pennsylvania smartweed, velvetleaf, and other weeds. The corn produces a high yield.

Example 4

An emulsifiable concentrate is prepared by stirring the ingredients listed below until solution is complete.

Linuron	14.8%
Propachlor	29.6%
Resorcinol	13.1%
Alkylarylsulfonate/ Polyoxyethylene alkylphenol condensate blend	4.0%
Trichloroethylene	38.5%

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Three kilograms of the above active ingredients are emulsified in 350 liters of water and applied pre-emergence to one hectare of sorghum. The treatment provides control of such weeds as crabgrass (<u>Digitaria sanguinalis</u>), giant foxtail (<u>Setaris magna</u>), common ragweed (<u>Ambrosia artemisiifolia</u>), and teaweed (<u>Sida spinosa</u>). The sorghum, free of weed competition, produces a good yield.

Example 5

An emulsifiable concentrate is prepared by stirring the ingredients listed below until solution is complete.

Linuron	11.4%
Propachlor	22.8%
Pheno1	6.5%
Polyoxyethylene ether/ polyoxyethylene glyceride/ alkylarylsulfonate blend	3.8%
Trichloroethylene	5 5 • 5%

Two kilograms of the above active ingredients are emulsified in 450 liters of water and applied as a directed post-emergence spray application to one hectare of soybeans. The treatment is applied when the soybean plants are 25 cm. tallor taller. The treatment provides control of barnyardgrass

(Echninochloa crusgalli), rough pigweed (Amaranthus retroflexus), giant foxtail (Setaria magna), and crabgrass (Digitaria sanguinalis).

Example 6

An emulsifiable concentrate is prepared by stirring the ingredients listed below until solution is complete.

Linuron	11.8%
Propachlor	23.6%
Polyoxyethylene sorbitol oleate/	3.7%
polyoxyethylene amine blend Chloroform	30.5%
1.1.2.2-tetrachloroethane	30.4%

Two and one quarter kilograms of the active ingredients are emulsified in 300 liters of water and applied to one hectare of sorghum planted in a Sassafras sandy loam soil. The treatment is applied pre-emergence to both the crop and weeds. Some of the weeds controlled include velvetleaf (Abutilon theophrasti), goosegrass (Eleusine indica), jimson weed (Datura stramonium), and curly duck (Rumex crispus).

Example 7

An emulsifiable concentrate is prepared by stirring the ingredients listed below until solution is complete.

Linuron	•	10.5%
Propachlor		21.0%
Dodecylbenzenesulfonic a	ıcid	13.8%
Chlorobenzene		54.7%

Three kilograms of the active components are emulsified in 450 liters of water and applied as a directed post-emergence spray application to one hectare of sorghum. The treatment is applied when the sorghum plants

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are 40 cm. tall or taller. The treatment controls crabgrass (Digitaria sanguinalis), yellow rocket (Barbarea vulgaris), rough pigweed (Amarnathus retroflexus) and giant foxtail (Setaria Magna). The sorghum continues to grow and produces a good crop.

Example 8

An emulsifiable concentrate is prepared by stirring the ingredients listed below until solution is complete.

	Linuron	9.1%
10	Propachlor	18.2%
	Polyoxyethylene sorbitol mono- oleste/polyoxyethylene amine blend	3.8%
	Benzyl alcohol	10.2%
	Trichloroethylene	58.7%

Three kilograms of the active ingredients are emulsified in 450 liters of water and applied as a directed post-emergence spray application to one hectare of corn growing in Matopeake silt loam soil. The treatment is applied when the corn plants are 40 cm. tall or taller. Many weeds are controlled including common ragweed (Ambrosia artemisiifolia), barnyard-grass (Echinochloa crusgalli), milkweed (Asclepias syriaca), and witchgrass (Panicium hemitomen). The corn, free of weed competition, continues to grow and produces a good crop.

Example 9

A solution suitable for direct application from low-volume equipment is prepared by combining the ingredients and stirring to form a solution.

		Linuron	12.0%
30		Propachlor	24.0%
•	term of	Dimethyl Formamide	64.0%

The above solution is applied pre-emergence to soybeans planted in Stanton silt loam soil at 9.5 liters per hectare. The treatment gives good control of crabgrass (<u>Digitaria spp.</u>), dallisgrass (<u>Paspalum dilitatum</u>), morning-glory (<u>Ipomoea spp.</u>), common ragweed (<u>Ambrosia artemisiifolia</u>) and many other serious weeds.

Example 10

A solution for direct application contains:

Linuron

9.1%

Propachlor

18.2%

Phenol

5.9%

Trichloroethylene

66.8%

applied pre-emergence to corn planted in Flanagan silt loam soil (high organic matter content). Many weed species are controlled, including pigweed (Amaranthus retroflexus), lambsquarter (Chenopodium album), great ragweed (Ambrosia trifida), Johnsongrass (Sorghum halepense), goosegrass (Eleusine indica) and cheat (Bromus secalinus). This treatment provides residual weed control allowing the corn to grow, free of weed competition, and produce a good yield.

Example 11

An emulsifiable concentrate is prepared by combining the ingredients listed below and stirring until solution is complete.

Linuron	9.1%
Propachlor	18.2%
Polyoxyethylene sorbitan mono- oleate	4.2%
Polyoxyethylene alkylaryl ether/ alkylarylsulfonate blend	2.8%
Phenol	5.9%
Trichloroethylene	59.8%

The above active ingredients are emulsified in water at a ratio of 1.5 kilograms per 100 liters of water. At a spray volume of 600 liters per hectare the emulsion is applied as a post-emergence spray application on annual weeds found growing in driveways, parking lots, around billboards, storage tanks, buildings and under pipelines. This treatment provides control of crabgrass (Digitaria spp.), pigweed (Amaranthus retroflexus), sheep sorel (Rumex acetosella), witchgrass (Panicum capillare), nutsedge (Cyperus spp.) and many other annual weeds. Residual control is obtained for several months.

CLAIMS

- 1. A liquid concentrate herbicidal formulation comprising from 15-50% of a mixture of 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea and 2-chloro-N-isopropylacetanilide, said compounds are present in a ratio of from 1 part by weight of 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea to 1 part by weight of 2-chloro-N-isopropylacetanilide to 1 part by weight of 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea to 3 parts by weight of 2-chloro-N-isopropylacetanilide and a suitable solvent system.
- 2. A formulation of Claim 1 in which the solvent is selected from the group consisting of an aromatic hydrocarbon, liquid aromatic halocarbon solvent and a liquid alignatic halocarbon solvent.
- 3. A liquid concentrate herbicidal formulation comprising from 15-50% of a mixture of 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea and 2-chloro-N-isopropylacetanilide, said compounds are present in a ratio of from 1 part by weight of 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea to 1 part by weight of 2-chloro-N-isopropylacetanilide to 1 part by weight of 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea to 3 parts by weight of 2-chloro-N-isopropylacetanilide; an effective amount of an emulsifying agent and the remainder of a suitable solvent; said formulation having a cloud point of 5°C. or lower.
- 4. A formulation of Claim 3 in which the solvent is selected from the group consisting of an aromatic hydrocarbon solvent, liquid aromatic halocarbon solvent and a liquid aliphatic halocarbon solvent.

- 5. A formulation of Claim 3 in which the solvent is an aromatic hydrocarbon within the distillation range of from 132°-371°C., is comprised of greater than 80% aromatics and has a flash point above 26°C.
- 6. A formulation of Claim 3 in which the solvent is an aromatic halocarbon.
- 7. A formulation of Claim 3 in which the solvent is an aliphatic halocarbon.
- 8. A liquid concentrate herbicidal formulation comprising from 15-50% of a mixture of 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea and 2-chloro-N-isopropylacetanilide, said compounds are present in a ratio of from 1 part by weight 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea to 1 part by weight 2-chloro-N-isopropylacetanilide to 1 part by weight 1-(3,4-dichlorophenyl)-3-methoxy-3-methylurea to 3 parts by weight 2-chloro-N-isopropylacetanilide; from 0-10% by weight of a suitable emulsifying agent; and from 40 to 85% by weight of a suitable solvent system comprised of from 100 to 60% major solvent and from 0 to 40% co-solvent; said formulation having a cloud point of 5°C. or lower.
 - 9. A formulation of Claim 8 in which the solvent is selected from the group consisting of an aromatic hydrocarbon solvent, liquid aromatic halocarbon solvent and a liquid alignatic halocarbon solvent.
 - 10. A formulation of Claim 8 in which the solvent is an aromatic hydrocarbon within the distillation range of from 132°-371°C., is comprised of greater than 80% aromatics and has a flash point above 26°C.

- 11. A formulation of Claim 8 in which the solvent is an aromatic halocarbon.
- 12. A formulation of Claim 8 in which the solvent is an aliphatic halocarbon.
- 13. A formulation of Claim 8 where the co-solvent when present is selected from the group consisting of an alkylbenzenesulfonic acid, and a phenol.
- 14. A formulation of Claim 9 where the co-solvent when present is selected from the group consisting of an alkylarylsulfonic acid, and a phenol.
- 15. A formulation of Claim 8 in which the co-solvent when present is selected from the group consisting of phenol, a cresol and resorcinol.
- 16. A formulation of Claim 9 in which the cosolvent when present is selected from the group consisting of phenol, a cresol and resorcinol.
- 17. A formulation of Claim 10 in which the cosolvent when present is selected from the group consisting of phenol, a cresol and resorcinol.
- 18. A formulation of Claim 11 in which the cosolvent when present is selected from the group consisting of phenol, a cresol and resorcinol.
- 19. A formulation of Claim 12 in which the cosolvent when present is selected from the group consisting of phenol, a cresol and resorcinol.

- 20. The formulation of Claim 9 in which the cosolvent when present is selected from the group consisting of dodecylbenzenesulfonic acid or nonylbenzenesulfonic acid.
- 21. A formulation of Claim 8 in which the cosolvent when present acts as the emulsifying agent.
- 22. A formulation of Claim 9 in which the cosolvent when present acts as the emulsifying agent.
- 23. A formulation of Claim 15 in which the active ingredient is present in a concentration of from 25-35% by weight.
- 24. A formulation of Claim 16 in which the active ingredient is present in a concentration of from 25-35% by weight.
- 25. A formulation of Claim 17 in which the active ingredient is present in a concentration of from 25-35% by weight.
- 26. A formulation of Claim 18 in which the active ingredient is present in a concentration of from 25-35% by weight.
- 27. A formulation of Claim 19 in which the active ingredient is present in a concentration of from 25-35% by weight.



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