(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 October 2006 (26.10.2006)

PCT

(10) International Publication Number
WO 2006/113320 A2

(51) International Patent Classification:
A01N 25/22 (2006.01)

(21) International Application Number:
PCT/US2006/013807

(22) International Filing Date: 12 April 2006 (12.04.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/671,127 14 April 2005 (14.04.2005) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/113320 A2

(54) Title: ALKYLBENZENES AND BOTTOMS PRODUCTS AS SOLVENT REPLACEMENT IN AGRICULTURAL APPLICATIONS

(57) Abstract: Embodiments of the present invention disclose a composition of matter useful in agricultural formulations comprising an agriculturally active ingredient and a hydrocarbon component having a bottoms product from the manufacture of alkylbenzene.

Alkylbenzenes and Bottoms Products as Solvent Replacement in Agricultural Applications

This invention relates generally to compositions of matter useful in agricultural applications. More particularly, it relates to aqueous emulsions and emulsifiable concentrates which contain an alkylbenzene bottoms material, preferably linear alkylbenzene bottoms material, in lieu of one or more solvents.

Background

Chemical formulations useful in the agricultural field are varied and many, and include those recognized by those skilled in the art as emulsions and emulsifiable concentrates from which emulsions may be conveniently prepared. Typically, a given volume of water is combined with an emulsifiable concentrate in order to yield a final end-use formulation which may be contained in a spray tank and applied directly to soil, insects, crops, and other foliage to exert a desired effect.

It is common in the art of emulsifiable concentrates which are useful in agricultural applications for such emulsifiable concentrates to include one or more organic solvents, for the purpose of dissolving one or more of the components of the emulsifiable concentrate, typically the agriculturally-active ingredient. Often, aromatic solvents such as those sold by ExxonMobil Chemical Co. under the names Aromatic and SOLVESSO™, including: Aromatic 100 solvent (C_8-C_{10}), Aromatic 150 solvent (C_{10}-C_{11}), Aromatic 200 solvent (C_{11}-C_{12}), SOLVESSO™ 100 solvent, SOLVESSO™ 150 fluid, and SOLVESSO™ 200 fluid, are employed. However, these solvents have drawbacks in that they have low flash points, are malodorous, and/or contain free naphthalene.

Summary of the Invention

Embodiments of the present invention include a composition of matter useful in agricultural formulations having at least one agriculturally active ingredient, and at least one hydrocarbon component. The hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes.

Additional embodiments include a composition of matter useful in agricultural formulations that have at least one agriculturally active ingredient and at least one hydrocarbon component, wherein the hydrocarbon component comprises at least 25% by weight of a mixture of mono-alkylbenzenes, wherein the structure of the mono-alkylbenzenes in the mixture include a single alkyl group bonded to a benzene ring, wherein the alkyl group may comprise any number of carbon atoms in the range of about 9 to about 42 carbon atoms.

The present invention also discloses an emulsified composition having a first portion of water; and a second portion of a composition having: at least one agriculturally active material; at least one hydrocarbon component, wherein the hydrocarbon component comprises a bottoms product from the manufacture of alkylbenzenes; and optionally one or more agricultural adjuvant materials.

The present invention further discloses a process for providing a composition suitable for being applied to crops, pests or soils which comprises providing a composition having at least one agriculturally active ingredient; and a hydrocarbon component, wherein the hydrocarbon component comprises a bottoms product from the manufacture of alkylbenzenes. The process then dilutes the composition with water.

Embodiments of the present invention further include an adjuvant made from an emulsifier, which may be a surfactant, and a hydrocarbon component, wherein the hydrocarbon component comprises a bottoms product from the manufacture of alkylbenzenes.

Other embodiments include a process for providing a composition suitable for use as an adjuvant by providing a composition comprising a hydrocarbon component, wherein the a hydrocarbon component comprises a bottoms product from the manufacture of alkylbenzenes; and contacting the composition with an emulsifier to form the adjuvant. In further embodiments the adjuvant is used in a spray application.

Detailed Description

The present invention is directed to compositions of matter useful in agricultural end-use applications and precursors therefor. A composition according to the invention includes a bottoms product from the manufacture of alkylbenzenes and linear alkylbenzenes as a replacement for one or more solvents which have heretofore been employed as solvents in emulsifiable concentrates in agricultural end-use applications.

The manufacture of alkyl benzenes and linear alkylbenzenes has been well-known in the art for quite some time and typically comprises as one step the alkylation of benzene to yield an alkylbenzene. It is known in the art to employ a mixture of C_8 and higher olefins which is to be combined with benzene in the presence of a suitable catalyst in order to afford a mixture of alkylbenzenes, which are subsequently removed from the reaction mixture, typically by one or more distillation steps, which leaves heavier-boiling materials behind while enabling the lighter alkylbenzenes to pass. Subsequently, the alkylbenzenes are sulfonated to provide linear alkylbenzene sulfonates, which are useful in detergents. The heavier-boiling materials left in the bottoms of the distillation apparatus are considered a scrap material which must be disposed of in an environmentally-acceptable fashion, which can sometimes be expensive.

Thus, during the manufacture of alkylbenzenes, a heavy-boiling material is accumulated during the distillation procedure as a "bottoms product". For purposes of this specification and the claims appended hereto the term "bottoms product" means the hydrocarbon materials produced during the manufacture of alkylbenzenes, which materials have a higher boiling point than the C_{14} fraction of mono alkylbenzene at a

pressure in the range of 10-50 mm Hg. In embodiments of the present invention, the bottoms product may have a higher boiling point than a C_{19} linear alkylbenzene at a pressure in the range of 10-50 mm Hg. Typically, such materials contain mono- and poly-alkyl benzenes produced as a by-product during the manufacture of mono-alkyl benzenes which are intended to be subsequently sulfonated and to be used either in detergent applications for household cleaning use or employment as detergents in engine oils. Examples of such "bottoms products" include MARLOTHERM® N heat transfer fluid from Sasol Olefins and Surfactants, GmbH of Bad Hamburg v. d. Höhe, Germany, and JEFFSOL® AG 5230 solvent available from Huntsman Petrochemical Corporation of The Woodlands, Texas.

The alkyl chains in the mixture of alkylbenzenes useful in accordance with the present invention may be linear or may contain branching on the alkyl chain or there may be multiple alkyl groups on the benzene ring itself. Thus, alkylated toluenes are within the scope of the term "bottoms product" in the present invention. Further, the use of alkylbenzenes as a solvent in agricultural end uses will contain various contents of different isomers that are all within the scope of the present invention.

The bottoms product may derive from an alkylbenzene process using C_{10} to C_{13} paraffin. The alkyl chains of the aklylbenzenes may be in the range of about C_9 to about C_{42}. In other embodiments, the range may be from about C_{10} to about C_{13}. In one embodiment, the range may be from about C_{11} to about C_{14}. In another embodiment, the range may be from about C_9 to about C_{15}. In other embodiments the range may be from about C_{19} to about C_{42}.

A bottoms product may include, but not be limited to, alkylbenzenes (of which some are tri-alkylbenzenes, di-alkylbenzenes, and mono-alkylbenzenes), alkylindanes and alkyltetralins, alkylindenes and alkyldialins, alkylnapthalenes,

diphenylalkanes, alkylacenapthenes, derivatives thereof and combinations thereof. A bottoms product may be a mixture of alkylbenzenes and alkylaromatics wherein the total carbon number for each individual molecule of alkylbenzene and alkylaromatic of the mixture is in the range of 18-44.

A bottoms product may have a bromine index in the range of about 0 to about 10,000. In another embodiment, the bromine index may be in the range of about 300 to about 1500. In some embodiments the bromine range may be from about 500 to about 700. The bromine index may be measured by electrometric titration with potassium bromide or potassium bromate solutions as used in ASTM D2710 or D5776.

We have found utility for the bottoms products and other products resulting from the manufacture of substantially linear or branched alkylbenzenes ("LAB") intended for use in making detergents as being suitable replacements for solvents commonly employed in producing emulsifiable concentrates for agricultural end uses. Thus, in one embodiment, a composition according to the present invention comprises: at least one agriculturally active ingredient, and at least one hydrocarbon component. The hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes. Optionally, the above embodiment may include at least one emulsifier. The emulsifier may be surfactant, such as blends of calcium dodecylbenzene sulfuric acid (DDBSA) and non-ionic surfactant. One skilled in the art will recognize appropriate surfactants to use in embodiments of the present invention. In addition, embodiments disclosed may include inert carriers, water, etc.

The present invention also discloses an emulsified composition having a first portion of water; and a second portion of a composition having: at least one

agriculturally active material; at least one hydrocarbon component, wherein the at least one hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes; and optionally one or more agricultural adjuvant materials.

The present invention further discloses a process for providing a composition suitable for being applied to crops, pests or soils which comprises providing a composition having at least one agriculturally active ingredient; and at least one hydrocarbon component, wherein the at least one hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes. The process then dilutes the composition with water. Such a composition may be applied directly to foliage, crops, animals, insects and/or soil. Such compositions may also be used for do-it-yourself home care products (i.e., bug sprays).

The present invention further discloses an adjuvant made out of an emulsifier, which may be surfactant, and a hydrocarbon component, wherein the hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes.

The present invention also discloses a process for providing an adjuvant by providing a composition comprising at least one hydrocarbon component, wherein the hydrocarbon component comprises a bottoms product from the manufacture of alkylbenzenes and contacting the composition with an emulsifier to form the adjuvant. In a further process, the adjuvant is then used in a spray application.

Agriculturally Active Materials

As used in this specification and the appended claims, the words "agriculturally active material" means any chemical substance that: 1) when applied to a given foliage that is generally regarded as undesirable adversely affects the

longevity and/or reproductive capability of such foliage; or 2) when applied to the vicinity where insects dwell adversely affects the longevity and/or reproductive capability of such insects; or 3) is regarded by those skilled in the art as possessing pesticidal (including either insecticidal or herbicidal) and/or fungicidal properties. Include within this definition, without limitation, are those chemical materials such as: 2,4,5-T, Acephate, Acetamiprid, Acetochlor, Acrinathrin, Aldicarb, Amitraz, Amitrole, Arsenic and its compounds, Bendiocarb, Benfuresate, Bensulfuron methyl, Bentazone, BHC, 2,4-D Bitertanol, Butamifos, Butylate, Cadusafos, Captafol(Difolatan), Captan, Carbaryl, Carfentrazone, Chinomethionat, Chlorfenvinphos, Chlorfluazuron, Chlorimuron ethyl, Chlormequat, Chlorobenzilate, Chlorpropham, Chlorpyrifos, Cinmethylin, Clofentezine, Copper terephthalate trihydrate, Cyanide compounds, Cyfluthrin, Cyhalothlin, Cyhexatin, Cypermethrin, Cyproconazole, Cyromazine, Daminozide, DCIP, DDT(including DDD,DDE), Deltamethrin, Demeton, Diazinon, Dicamba, Dichlofluanid, Dichlorvos, Diclomezine, Dicofol(Kelthane), Dieldrin(including Aldrin), Diethofencarb, Difenoconazole, Difenzoquat, Diflubenzuron, Dimethipin, Dimethoate, Dimethylvinphos, Dithiopyr, Edifenphos, Endrin, EPN, EPTC, Esprocarb, Ethiofencarb, Ethofenprox, Ethoprophos, Ethoxyquin, Etobenzanide, Etrimfos, Fenarimol, Fenbutatin oxide, Fenitrothion, Fenobucarb, Fenpyroximate, Fensulfothion, Fenthion, Fenvalerate, Flucythrinate, Flufenoxuron, Fluoroimide, Flusilazole, Flusulfamide, Flutolanil, Fluvalinate, Fosetyl, Fosthiazate, Glufosinate, Glyphosate, Guthion, Halfenprox, Heptachlor (including Heptachlor epoxide), Hexaflumuron, Hexythiazox, Imazalil, Imazosulfuron, Imibenconazole, Iminoctadine, Inabenfide, Inorganic bromide, Iprodione, Isophenphos, Isoprocarb, Lead & its compounds, Lenacil, Malathion, Maleic hydrazide, MCPA (including Phenothiol), Mepanipyrim, Mephenacet,

Mepronil, Methamidophos, Methiocarb, Methoprene, Methoxychlor, Metolachlor, Metribuzin, Mirex, Myclobutanil, Nitenpyram, Oxamyl, Paclobutrazol, Parathion, Parathion-methyl, Pencycuron, Pendimethalin, Permethrin, Phenthoate, Phosalone(Rubitox), Phoxim, Picloram, Pirimicarb, Pirimiphos-methyl, Pretilachlor, Prohexadione, Propamocarb, Propiconazole, Prothiofos, Pyraclofos, Pyrazoxyfen, Pyrethrins, Pyridaben, Pyridate, Pyrifenox, Pyrimidifen, Pyriproxyfen, Quinalphos, Quinclorac, Sethoxydim, Silafluofen, Tebuconazole, Tebufenozide, Tebufenpyrad, Tecloftalam, Tefluthrin, Terbufos, Thenylchlor, Thiobencarb, Thiometon, Tralomethrin, Triadimenol, Tribenuron methyl, Trichlamide, Trichlorfon, Triclofos-methyl, Tricyclazole, Triflumizole, Trifluralin and Vamidothion, derivatives thereof and combinations thereof.

Agricultural Adjuvants

Adjuvants are chemical materials which are often employed as a component of an agriculturally active material, and which are designed to perform specific functions, including wetting, spreading, sticking, reducing evaporation, reducing volatilization, buffering, emulsifying, dispersing, reducing spray drift, compatibilizing and reducing foaming. No single adjuvant can perform all these functions, but different compatible adjuvants often can be combined to perform multiple functions simultaneously; thus, adjuvants are a diverse group of chemical materials. Within the meaning of the term "Adjuvants" is included any substance added to a spray tank to modify a pesticide's performance, the physical properties of the spray mixture, or both.

Spray application is perhaps the weakest link in the chain of events a pesticide follows through its development process. Some researchers claim that up to 70

percent of the effectiveness of a pesticide depends on the effectiveness of the spray application. Selection of a proper adjuvant may reduce or even eliminate spray application problems associated with pesticide stability, solubility, incompatibility, suspension, foaming, drift, evaporation, volatilization, degradation, adherence, penetration, surface tension, and coverage, thereby improving overall pesticide efficiency and efficacy.

Surfactant adjuvants physically alter the surface tension of a spray droplet. For a pesticide to perform its function properly, a spray droplet must be able to wet the foliage and spread out evenly over a leaf. Surfactants enlarge the area of pesticide coverage, thereby increasing the pest's exposure to the chemical. Without proper wetting and spreading, spray droplets often run off or fail to adequately cover these surfaces. Such materials enhance the absorbing, emulsifying, dispersing, spreading, sticking, wetting or penetrating properties of pesticides. Surfactants are most often used with herbicides to help a pesticide spread over and penetrate the waxy outer layer of a leaf or to penetrate through the small hairs present on a leaf surface.

While surfactant adjuvants may be anionic, cationic, or nonionic, the nonionic surfactants are in most common usage. The "multi-purpose" nonionic surfactants are generally composed of alkoxylates of alcohols and alkoxylates of fatty acids, have no electrical charge and are compatible with most pesticides. Certain other surfactants may be cationic (+ charge) or anionic (- charge) and there are specialty adjuvants that are used in certain situations and with certain products. Anionic surfactants are used in emulsifier blends, and some chemistries are more specialized and used as dispersants and compatibility agents. Cationic surfactants are used less frequently but one group, the ethoxylated fatty amines, sometimes are used with the herbicide glyphosate.

Silicone-based surfactants have found some use due to their superior spreading ability. Some of these surfactants are a blend of nonionic surfactants (NIS) and a silicone surfactant while others are entirely a silicone chemistry. The combination of a NIS and a silicone surfactant can increase absorption into a plant so that the time between application and rainfall can be shortened. There are generally two types of organo-silicone surfactants: the polyether-silicones that are soluble in water and the alkyl-silicones that are soluble in oil. Unlike polyether-silicone types, alkyl-silicone surfactants work well with oil-based sprays, such as dormant and summer oil sprays used in insect control. Alkyl-silicone-enhanced oil sprays can maximize insecticidal activity and even allow significantly lower pesticide use rates that reduce residue levels on crops.

Sticker adjuvants increase the adhesion of solid particles to target surfaces. These adjuvants can decrease the amount of pesticide that washes off during irrigation or rain. Stickers also can reduce evaporation of the pesticide and some slow ultraviolet (UV) degradation of pesticides. Many adjuvants are formulated as spreader-stickers to make a general purpose product that includes a wetting agent and an adhesive.

Extender adjuvants function like sticker surfactants by retaining pesticides longer on the target area, slowing volatilization, and inhibiting UV degradation.

Plant penetrant adjuvants have a molecular configuration that enhances penetration of some pesticides into plants. An adjuvant of this type may increase penetration of a pesticide on one species of plant but not another. Systemic herbicides, auxin-type herbicides, and some translocatable fungicides can have their activity increased as a result of enhanced penetration.

Compatibility agent adjuvants are especially useful when pesticides are combined with liquid fertilizers or other pesticides, particularly when the combinations are physically or chemically incompatible, such as in cases when clumps and/or uneven distribution occurs in the spray tank. A compatibility agent may eliminate problems associated with such situations.

Buffers or pH modifier adjuvants are generally employed to prevent problems associated with alkaline hydrolysis of pesticides that are encountered when the pH of a pesticide exceeds about 7.0 by stabilizing the pH at a relatively constant level. Extreme pH levels in the spray mixture can cause some pesticides to break down prematurely. This is particularly true for the organophosphate insecticides but some herbicides can break down into inactive compounds in a matter of hours or minutes in alkaline situations (pH>7). For example, the insecticide Cygon (dimethoate) loses 50 percent of its pest control power in just 48 minutes when mixed in water of pH 9. At a pH of 6, however, it takes 12 hours for degradation to progress to that extent. On the other hand, sulfonyl urea (SU) herbicides tend to break down more rapidly where the pH is below 7. At low pHs, the herbicide 2,4-D (acid form) is an uncharged molecule. At higher pH, 2,4-D tends to become more anionic, and more water-soluble, which can affect its movement in the environment. Leaf coatings often have a high pH that can contribute to poor performance with certain herbicides. The use of a buffering or acidifying adjuvant can stabilize or lower the pH of a spray solution thereby improving the stability of the pesticide being used.

Mineral control adjuvants are used to mask the problems associated with water hardness minerals in spray water which can diminish the effectiveness of many pesticides. Mineral ions such as calcium, magnesium, iron, salts and carbonates are commonly found in hard water. These ions can bind with the active ingredients of

some pesticides, especially the salt-formulation herbicides such as ROUNDUP® herbicide (glyphosate), POAST® herbicide (sethoxydim), PURSUIT® herbicide (imazethapyr), and LIBERTY® herbicide (glufosinate) resulting in poor weed control. ROUNDUP is a registered mark of Monsanto Technology LLC of St. Louis, Missouri. POAST is a registered mark of BASF Aktiengesellschaft of Ludwigshafen, Germany. PURSUIT is a registered mark of the American Cyanamid Company of Wayne, New Jersey. LIBERTY is a registered mark of Bayer CropScience LP of Research Triangle Park, North Carolina. The use of water-conditioning adjuvants gives hard water minerals something to bind with other than the herbicide. In addition, some ammonium sulfate-based adjuvants can be used to offset hard water problems.

Drift retardant adjuvants improve on-target placement of pesticide spray by increasing the average droplet size, since drift is a function of droplet size with drops with diameters of 100 microns or less tending to drift away from targeted areas.

Defoaming agent adjuvants are used to control the foam or frothy head often present in some spray tanks that results from the surfactant used and the type of spray tank agitation system can often can be reduced or eliminated by adding a small amount of foam inhibitor.

Thickener adjuvants increase the viscosity of spray mixtures which afford control over drift or slow evaporation after the spray has been deposited on the target area.

Oil-based adjuvants have been gaining in popularity especially for the control of grassy weeds. There are three types of oil-based adjuvants: crop oils, crop oil concentrates (COC) and the vegetable oils. Crop Oil adjuvants are derivative of paraffin-based petroleum oil. Paraffinic crop oils are generally 95-98% oil with 1 to

2% surfactant/emulsifier. Crop oils promote the penetration of a pesticide spray either through a waxy plant cuticle or through the tough chitinous shell of insects. Crop oils may also be important in helping solubilize less water-soluble herbicides such as POAST® (sethoxydim), FUSILADE® herbicide (fluaziprop-butyl) and atrazine. FUSILADE is a registered mark of Imperial Chemical Industries PLC of London, England. Traditional crop oils are more commonly used in insect and disease control than with herbicides. Crop oil concentrates (COC) are a blend of crop oils (80-85%) and the nonionic surfactants (15-20%). The purpose of the nonionic surfactant in this mixture is to emulsify the oil in the spray solution and lower the surface tension of the overall spray solution. Vegetable oils work best when their lipophilic characteristics are enhanced, and one common method of achieving this is by esterification of common seed oils such as rapeseed, soybean, and cotton. The methylated seed oils (MSO) are comparable in performance to the crop oil concentrates, in that they increase penetration of the pesticide. In addition, silicone-based MSOs are also available that take advantage of the spreading ability of the silicone surfactant and the penetrating characteristics of the MSOs.

The special purpose or utility adjuvants are used to offset or correct certain conditions associated with mixing and application such as impurities in the spray solution, extreme pH levels, drift, and compatibility problems between pesticides and liquid fertilizers. These adjuvants include acidifiers, buffering agents, water conditioners, anti-foaming agents, compatibility agents, and drift control agents.

Fertilizer-based adjuvants, particularly nitrogen-based liquid fertilizers, have been frequently added to spray solutions to increase herbicide activity. Research has shown that the addition of ammonium sulfate to spray mixtures enhances herbicidal activity on a number of hard-to-kill broadleaf weeds. Fertilizers containing

ammonium nitrogen have increased the effectiveness of the certain polar, weak acid herbicides such as ACCENT® herbicide (nicosulfuron), BANVEL® herbicide (dicamba), BLAZER® herbicide (acifluorfen-sodium), ROUNDUP® herbicide (glyphosate), BASAGRAN® herbicide (bentazon), POAST® herbicide (sethoxydim), PURSUIT® herbicide (imazethapyr), and 2,4-D amine. ACCENT is a registered mark of E.I. du Pont de Nemours and Company. BANVEL-K is a registered mark of Sandoz AG, Basel, Switzerland. BLAZER is the registered mark of Rohm and Haas Company of Philadelphia, Pennsylvania. BASAGRAN is a registered mark of BASF Aktiengesellschaft of Ludwigshafen, Germany. Early fertilizer-based adjuvants consisted of dry (spray-grade) ammonium sulfate (AMS) at 17 lbs per 100 gallons of spray volume (2%). Studies of these adjuvants have shown improved ROUNDUP® herbicide efficacy. The improvements were most pronounced in spray water containing relatively large quantities of certain hard water ions, such as calcium and magnesium. It is thought that the ions in the fertilizer tied up or chelated the hard water ions thereby enhancing herbicidal action.

Thus, the words "agricultural adjuvant" when used in this specification and the appended claims means any material recognized by those skilled in the art of pesticides to be useful as an adjuvant material in connection with the formulation and/or use of a pesticide, and include all materials falling within the specific classes outlined above.

One characteristic of a bottoms product of LAB manufacture such as Huntsman Petrochemical Corporation's JEFFSOL® AG 5230 solvent or MARLOTHERM® N heat transfer fluid and its analogs, is that these materials are not volatile aromatic solvents, but rather they comprise characteristics of both aromatic and aliphatic hydrocarbons. One illustrative example is that propylene carbonate is

completely miscible in aromatic hydrocarbons, but is completely immiscible in aliphatic hydrocarbons. However, propylene carbonate is very slightly soluble (0.5%) in JEFFSOL® AG 5230 solvent. Thus, JEFFSOL® AG 5230 solvent behaves almost as a crop oil (aliphatic), but possesses some aromatic character. Since they are non-volatile, regulatory VOC issues are wholly minimized.

The bottoms products of LAB manufacture are well-suited to function as replacement solvents for other alkyl benzene types, which are commonly referred to as Aromatic distillates, which are exemplified by the products Aromatic 100 solvent, Aromatic 150 solvent, and Aromatic 200 solvent, all available from the ExxonMobil Chemical Company, and including like products.

A popular emulsifier useful for formulating crop oils is sold by Huntsman Petrochemical Corporation of The Woodlands, Texas under the trade name of SURFONIC® AG-800 adjuvant. Blending about 10-15 parts by weight of SURFONIC® AG-800 adjuvant with 85-90 parts by weight of JEFFSOL® AG 5230 solvent or MARLOTHERM® N heat transfer fluid provides a mixture which could be regarded as a crop oil concentrate to which an agriculturally-active material may be subsequently added, along with one or more optional adjuvant materials, to provide a composition according to the invention, which is an emulsifier package.

Another popular emulsifier available from Huntsman Petrochemical Corporation of The Woodlands, Texas is sold under the trade name of SURFONIC® AG-347 adjuvant. Blending about 10-15 parts by weight of SURFONIC® AG-347 adjuvant with 85-90 parts by weight of JEFFSOL® AG 5230 solvent or MARLOTHERM® N heat transfer fluid provides a mixture which could be regarded as a crop oil concentrate to which an agriculturally-active material may be

subsequently added, along with one or more optional adjuvant materials, to provide a composition according to an alternative embodiment of the present invention, which is an emulsifier package.

The examples below are two examples of actives dissolved in JEFFSOL® AG 5230 solvent with different ratios of emulsifiers. These examples are to be construed as illustrative of the present invention and in no way delimitive thereof.

Trifluralin

A trifluralin solvent stock solution was prepared by dissolving 75 grams of trifluralin in 225 grams of JEFFSOL® AG 5230 solvent solvent to make a 25% (w/w) trifluralin solution. This stock solution was used in turn to produce the Emulsifier Stock Solutions specified below:

Emulsifier Stock Solution 1 - 5 grams of NANSA® EVM70/2E surfactant (Huntsman Petrochemical Corporation) was dissolved in 45 grams of trifluralin stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 2 - 5 grams of tall oil fatty acid (TOFA) (commercially available from Arizona Chemical of Jacksonville, Florida) was dissolved in 45 grams of trifluralin stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 3 - 5 grams of SURFONIC® L24-5 surfactant (Huntsman Petrochemical Corporation) was dissolved in 45 grams of trifluralin stock solution to produce a 10% emulsifier stock solution.

Working Solution 1 - A working solution was prepared by combining and mixing, in a 20-milliliter (ml) glass vial: 3.3 grams of emulsifier stock solution 1; 3.3 grams emulsifier stock solution 2; and 3.4 grams of emulsifier stock solution 3. This

working solution contains 10% of the emulsifier blend above in a 22.5% trifluralin solution.

Final Formulations - 99 ml of water were added to each of three separate 100 ml Nessler tubes. The hardness of the water in each tube was 34 parts per million (ppm), 342 ppm and 1000 ppm respectively, as measured using World Health Organization guidelines of determining water hardness. One milliliter of Working Solution 1 was added to each tube and observed for bloom. The tubes were inverted 10 times to ensure mixing, then observed for emulsion quality for 1 hour. The emulsion quality in each of the examples' final formulations was graded using the following scale: "Excellent" represents milky white properties and observed bluish haze on sides of tubes when inverted; "Good" represents milky white properties with no bluish haze noted during inversion; "Poor" represents phase separation indicated by a cream layer or oil layer separated from the water portion.

Permethrin

A permethrin Solvent Stock Solution was prepared by dissolving 135 grams of permethrin in 165 grams of JEFFSOL® AG 5230 solvent to make a 45% (w/w) permethrin solution. This stock solution was used in turn to produce the Emulsifier Stock Solutions specified below.

Emulsifier Stock Solution 4 – 5 grams of NANSA® EVM70/2E surfactant was dissolved in 45 grams of permethrin stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 5 – 5 grams of TOFA was dissolved in 45 grams of permethrin stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 6 – 5 grams of SURFONIC® L24-5 surfactant was dissolved in 45 grams of permethrin stock solution to produce a 10% emulsifier stock solution.

Working Solution 2 - A working solution was prepared by combining and mixing, in a 20-ml glass vial: 3.3 grams of emulsifier stock solution 4; 3.3 grams of TOFA emulsifier stock solution 5; and 3.4 grams of emulsifier stock solution 6. This working solution contains 3.3% of each emulsifier mentioned above in a 40.5% permethrin solution.

Final Formulations - 99 ml of water were added to each of three separate 100 ml Nessler tubes. The hardness of the water in each tube was 34 ppm, 342 ppm and 1000 ppm respectively, as measured using World Health Organization guidelines of determining water hardness. One milliliter of Working Solution 2 was added to each tube and observed for bloom. The tubes were inverted 10 times to ensure mixing, then observed for emulsion quality for 1 hour.

Acetochlor

An acetochlor stock solution was prepared by dissolving 135 grams of acetochlor in 165 grams of JEFFSOL® AG 5230 solvent to make a 45% (w/w) acetochlor solution. This stock solution was used in turn to produce the Emulsifier Stock Solutions specified below.

Emulsifier Stock Solution 7 – 5 grams of NANSA® EVM70/2E surfactant was dissolved in 45 grams of acetochlor stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 8 – 5 grams of TOFA was dissolved in 45 grams of acetochlor stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 9 – 5 grams of SURFONIC® L24-5 surfactant was dissolved in 45 grams of acetochlor stock solution to produce a 10% emulsifier stock solution.

Working Solution 3 - A working solution was made by combining, in a 20-ml glass vial, 3.3 grams of emulsifier stock solution 7; 3.3 grams of TOFA emulsifier stock solution 8; and 3.4 grams of emulsifier stock solution 9, and mixed well. This working solution contains 3.3% of each emulsifier mentioned above in a 40.5% Acetochlor solution.

Final Formulations - 99 ml of water were added to each of three separate 100 ml Nessler tubes. The hardness of the water in each tube was 34 ppm, 342 ppm and 1000 ppm respectively, as measured using World Health Organization guidelines of determining water hardness. One milliliter of Working Solution 3 was added to each tube and observed for bloom. The tubes were inverted 10 times to ensure mixing, then observed for emulsion quality for 1 hour.

Chlorpyrifos

A chlorpyrifos stock solution was prepared by dissolving 135 grams of chlorpyrifos in 165 grams in JEFFSOL® AG 5230 solvent to make a 45% (w/w) chlorpyrifos solution. This stock solution was used in turn to produce the emulsifier stock solutions specified below.

Emulsifier Stock Solution 10 – 5 grams of NANSA® EVM70/2E surfactant was dissolved in 45 grams of Chlorpyrifos stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 11 – 5 grams of TOFA (Tall Oil Fatty Acid-Arizona Chemical) was dissolved in 45 grams of Chlorpyrifos stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 12 – 5 grams of SURFONIC® L24-5 surfactant was dissolved in 45 grams of Chlorpyrifos stock solution to produce a 10% emulsifier stock solution.

Working Solution 4 - A working solution was made by combining, in a 20-ml glass vial, 3.3 grams of stock solution 10; 3.3 grams of emulsifier stock solution 11; and 3.4 grams of emulsifier stock solution 12, and mixed well. This working solution contains 3.3% of each emulsifier mentioned above in a 40.5% Chlorpyrifos solution.

Final Formulations - 99 ml of water were added to each of three separate 100 ml Nessler tubes. The hardness of the water in each tube was 34 ppm, 342 ppm and 1000 ppm respectively, as measured using World Health Organization guidelines of determining water hardness. One milliliter of Working Solution 4 was added to each tube and observed for bloom. The tubes were inverted 10 times to ensure mixing, then observed for emulsion quality for 1 hour.

Dithiopyr

A dithiopyr stock solution was prepared by dissolving 30 grams of dithiopyr in 270 grams of JEFFSOL® AG 5230 solvent to make a 10% (w/w) dithiopyr solution. This stock solution was used in turn to produce the Emulsifier Stock Solutions specified below.

Emulsifier Stock Solution 13 – 5 grams of NANSA® EVM70/2E surfactant was dissolved in 45 grams of Dithiopyr stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 14 – 5 grams of TOFA was dissolved in 45 grams of Dithiopyr stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 15 – 5 grams of SURFONIC® L24-5 surfactant was dissolved in 45 grams of Dithiopyr stock solution to produce a 10% emulsifier stock solution.

Working Solution 5 – A working solution was made by combining, in a 20-ml glass vial, 3.3 grams of emulsifier stock solution 13; 3.3 grams of emulsifier stock solution 14; and 3.4 grams of emulsifier stock solution 15, and mixed well. This working solution contains 3.3% of each emulsifier mentioned above in a 9% Dithiopyr solution.

Final Formulations - 99 ml of water were added to each of three separate 100 ml Nessler tubes. The hardness of the water in each tube was 34 ppm, 342 ppm and 1000 ppm respectively, as measured using World Health Organization guidelines of determining water hardness. One milliliter of Working Solution 5 was added to each tube and observed for bloom. The tubes were inverted 10 times to ensure mixing, then observed for emulsion quality for 1 hour.

Carfentrazone

A carfentrazone stock solution was prepared by dissolving 30 grams of carfentrazone in 270 grams of JEFFSOL® AG 5230 solvent to make a 10% (w/w) carfentrazone solution. This stock solution was used in turn to produce the Emulsifier Stock Solutions specified below.

Emulsifier Stock Solution 16 – 5 grams of NANSA® EVM70/2E surfactant was dissolved in 45 grams of Carfentrazone stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 17 – 5 grams of TOFA was dissolved in 45 grams of Carfentrazone stock solution to produce a 10% emulsifier stock solution.

Emulsifier Stock Solution 18 – 5 grams of SURFONIC® L24-5 surfactant was dissolved in 45 grams of Carfentrazone stock solution to produce a 10% emulsifier stock solution.

Working Solution 6 – A working solution was made by combining, in a 20-ml glass vial, 3.3 grams of NANSA® EVM 70/2E emulsifier stock solution was mixed with 3.3 grams of TOFA emulsifier stock solution and 3.4 grams of SURFONIC® L-24-5 surfactant emulsifier stock solution and mixed well. This working solution contains 3.3% of each emulsifier mentioned above in a 9% carfentrazone solution.

Final Formulations - 99 ml of water were added to each of three separate 100 ml Nessler tubes. The hardness of the water in each tube was 34 ppm, 342 ppm and 1000 ppm respectively, as measured using World Health Organization guidelines of determining water hardness. One milliliter of Working Solution 6 was added to each tube and observed for bloom. The tubes were inverted 10 times to ensure mixing, then observed for emulsion quality for 1 hour.

After addition of the emulsifiable concentrate to the water, each sample formulation was checked for bloom, emulsification and stability in 34 ppm, 342 ppm and 1000

ppm water hardness. Stability measurements were made after 1 hour. Results of observations for the foregoing 6 examples are tabulated in Table I below:

Example Mat'l.	H_2O hardness	Bloom	Emulsion	1-hr stability
trifluralin				
	34	excellent	excellent	excellent
	342	excellent	excellent	excellent
	1000	excellent	excellent	good
permethrin				
	34	excellent	excellent	excellent
	342	excellent	excellent	excellent
	1000	excellent	excellent	good
acetochlor				
	34	excellent	excellent	excellent
	342	excellent	excellent	good
	1000	excellent	excellent	good
chlorpyrifos				
	34	excellent	excellent	excellent
	342	excellent	excellent	excellent
	1000	excellent	excellent	good
dithiopyr				
	34	excellent	excellent	excellent
	342	excellent	excellent	excellent
	1000	excellent	excellent	good
carfentrazone				
	34	excellent	excellent	excellent
	342	excellent	excellent	excellent
	1000	excellent	excellent	good

Table I

"good" = milky white properties with no bluish haze noted during inversion.

"excellent" = milky white properties and observed bluish haze on sides of tubes when inverted.

The solubilities of some active ingredients in LAB bottoms is shown below in Table II:

LAB Solubility Table	
Active	**JEFFSOL® AG 5230 solvent**
Trifluralin	200 g/l
Bifenthrin 96.4%	nd
Permethrin 92%	>450 g/l
Deltamethrin	<50 g/L
Quizalofop-ethyl 98%	nd
Chlorpyrifos 98%	> 450 g/l
Metolachlor 95%	> 450 g/l
Dithiopyr 90%	150 g/l
Carfentrazone 91.3%	150 g/l
Pendimethalin	250 g/l
Flumethrin	250 g/l
Acetochlor 95.7%	>450 g/l
Diazinon 91.6%	>450 g/l

Table II – solubilities of some active materials in linear alkylbenzene materials

Consideration must be given to the fact that although this invention has been described and disclosed in relation to certain preferred embodiments, obvious equivalent modifications and alterations thereof will become apparent to one of ordinary skill in this art upon reading and understanding this specification and the claims appended hereto. The present disclosure includes the subject matter defined by any combination of any one of the various claims appended hereto with any one or more of the remaining claims, including the incorporation of the features and/or limitations of any dependent claim, singly or in combination with features and/or limitations of any one or more of the other dependent claims, with features and/or limitations of any one or more of the independent claims, with the remaining dependent claims in their original text being read and applied to any independent claim so modified. This also includes combination of the features and/or limitations

of one or more of the independent claims with the features and/or limitations of another independent claim to arrive at a modified independent claim, with the remaining dependent claims in their original text being read and applied to any independent claim so modified. Accordingly, the presently disclosed invention is intended to cover all such modifications and alterations, and is limited only by the scope of the claims which follow, in view of the foregoing and other contents of this specification.

What is claimed is:

1) A composition of matter useful in agricultural formulations comprising:

a) at least one agriculturally active ingredient;

b) at least one hydrocarbon component, wherein the hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes.

2) A composition according to claim 1 wherein the manufacture of alkylbenzenes comprises the manufacture of linear alkylbenzenes.

3) A composition according to claim 1 wherein the bottoms product has a higher boiling point than a C_{14} fraction of mono alkylbenzene at a pressure in the range of 10-50 mm Hg.

4) A composition according to claim 1 wherein the bottoms product has a higher boiling point than a C_{19} linear alkylbenzene at a pressure in the range of 10-50 mm Hg.

5) A composition according to claim 1 further comprising at least one emulsifier.

6) A composition according to claim 1 wherein the bottoms product comprises a mono-alkyl benzene.

7) A composition according to claim 1 wherein the bottoms product comprises a di-alkyl benzene.

8) A composition according to claim 1 wherein the bottoms product comprises a tri-alkyl benzene.

9) A composition according to claim 1 wherein the bottoms product has a bromine index in the range of about 0 to about 10,000.

10) A composition according to claim 1 wherein the bottoms product has a bromine index in the range of about 300 to about 1500.

11) A composition according to claim 1 wherein the bottoms product has a bromine index in the range of about 500 to about 700.

12) A composition according to claim 1 wherein the bottoms product comprises a mixture of alkylbenzenes and alkylaromatics wherein the total carbon number is in the range of 18 to 44.

13) A composition according to claim 1 wherein the bottoms product comprises an akylbenzene with an alkyl chain in the range of about C_9 to about C_{42}.

14) A composition according to claim 1 wherein the bottoms product comprises an akylbenzene with an alkyl chain in the range of about C_9 to about C_{15}.

15) A composition according to claim 1 wherein the bottoms product comprises an akylbenzene with an alkyl chain in the range of about C_{10} to about C_{13}.

16) A composition according to claim 1 wherein the bottoms product comprises an akylbenzene with an alkyl chain in the range of about C_{11} to about C_{14}.

17) A composition according to claim 1 wherein the bottoms product comprises an akylbenzene with an alkyl chain in the range of about C_{19} to about C_{42}.

18) A composition of matter useful in agricultural formulations which comprises:

a) at least one agriculturally active ingredient;

b) at least one hydrocarbon component, wherein the at least one hydrocarbon component comprises at least 25% by weight of a mixture of mono-alkylbenzenes, wherein the structure of the mono-alkylbenzenes in the mixture include a single alkyl group bonded to a benzene ring, wherein the alkyl group may comprise any number of carbon atoms in the range of about 9 to about 42 carbon atoms.

19) A composition according to claim 18 further comprising at least one emulsifier.

20) A composition according to claim 18 wherein the alkyl group may comprise any number of carbon atoms in the range of about 9 to about 15 carbon atoms.

21) A composition according to claim 18 wherein the alkyl group may comprise any number of carbon atoms in the range of about 10 to about 13 carbon atoms.

22) A composition according to claim 18 wherein the alkyl group may comprise any number of carbon atoms in the range of about 19 to about 42 carbon atoms.

23) An emulsified composition comprising:

a) a first portion of water; and

b) a second portion of a composition which comprises:

i) at least one agriculturally active ingredient;

ii) at least one hydrocarbon component, wherein the hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes; and

iii) optionally one or more agricultural adjuvant materials.

24) A process for providing a composition suitable for being applied to crops, pests or soils which comprises the steps of:

a) providing a composition comprising:

i) at least one agriculturally active ingredient;

ii) at least one hydrocarbon component, wherein the hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes; and

b) diluting the composition with water.

25) A composition of matter useful as an adjuvant comprising:

i) at least one emulsifier;

ii) at least one hydrocarbon component, wherein the hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes.

26) A composition according to claim 25 wherein the emulsifier is a surfactant.

27) A process for providing a composition suitable for use as an adjuvant which comprises the steps of:

a) providing a composition comprising at least one hydrocarbon component, wherein the hydrocarbon component comprises at least one bottoms product from the manufacture of alkylbenzenes; and

b) contacting the composition with an emulsifier to form the adjuvant.

28) A process according to claim 27 further comprising using the adjuvant in a spray application.