

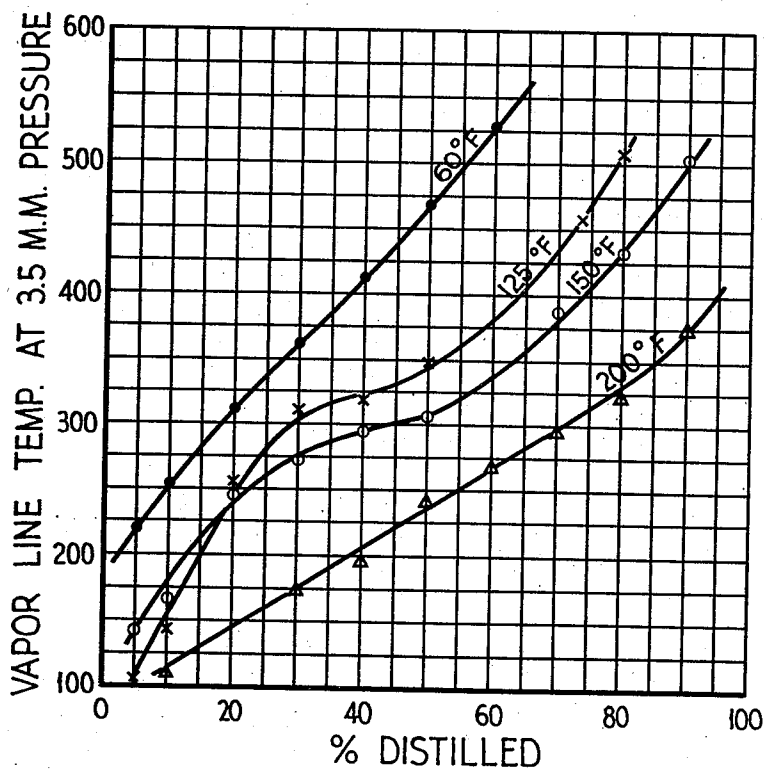
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PARASITICIDAL SPRAY OIL COMPOSITION

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PARASITICIDAL SPRAY OIL COMPOSITION

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10 Claims. (Cl. 167—28)

This invention relates to parasiticial spray oil compositions for the control of insect and fungus pests on growing vegetation and to methods of preparing such compositions.

5 This application is a part continuation of my application for United States Letters Patent Serial No. 653,272, filed January 24, 1933.

It has been the aim of this branch of the insecticidal and fungicidal art to provide materials which, upon proper application to growing plant foliage, would fulfill their insecticidal and fungicidal purposes without damage or injury to the foliage or prejudice to fruition. Of late years this aim or ideal has been closely approximated by the controlled use of highly refined petroleum oils, either in emulsified or diluted form or in very finely divided spray or mist form, and such highly refined petroleum oils are now in wide and accepted use on the most delicate plant foliage during the growing seasons. The satisfactory use of these highly refined petroleum oils has been made possible by the discovery that certain constituents of crude or moderately refined naturally occurring petroleum oils, notably aromatic and unsaturated hydrocarbons, sulfur compounds and organic acids, are distinctly injurious to growing plant foliage, and that the removal of these types of harmful or phytocidal compounds from petroleum oils provides an oil that may be used with safety. Unfortunately these harmful types of compounds, although present in petroleum oils in but relatively small proportions, are exceedingly difficult to remove, and recourse has perforce been had to drastic chemical treatment, as with strong sulfuric acid, or to the equally drastic selective solvent refining types of treatment, the latter followed in many cases by treatment with strong sulfuric acid, for their removal.

40 Of the several types of compounds enumerated above as those considered phytocidal by the parasiticial art, the unsaturated hydrocarbons as a class are the most difficult to remove from crude petroleum oils or their distillates. Thus in the ordinary preparation of these oils for insecticidal uses the measurement of their "unsaturated content" is considered of first importance, for by the time the unsaturated content has been reduced to an acceptable figure, the oil is already sufficiently free of other harmful types of compounds to be used with safety on growing plant foliage. In the trade, the absence of harmful types of compounds is recognized and measured by the term "unsulfonated residue",—the percent
55 by volume of an oil remaining inert to treatment

with four times its volume of 37N H₂SO₄ for one hour at 100° C.,—the degree of freedom from unsaturated or sulfonatable hydrocarbons increasing as "unsulfonated residue" increases and a complete freedom being recognized by the term "unsulfonated residue 100%". The significance attached to freedom from unsaturated or sulfonatable constituents in a parasiticial mineral or petroleum oil is legally recognized in many areas, to the extent that such oils when sold for use in pest control during foliage growing or fruition seasons, whether or not admixed with other materials, must be labelled with the minimum guaranteed percentage of unsulfonated residue. In arid and semi-arid regions, petroleum oil spray manufacturers do not now ordinarily market an oil for summer use with an unsulfonated residue below about 90%, and many of the oils intended for summer use have unsulfonated residues of 97–100%.

The difficulty and expense involved in the preparation of oils of such high purity from naturally occurring crude petroleum or their distillates will be appreciated by reference to the fact that oils with unsulfonated residues of 100% are of essentially "white oil" grade, and that oils as highly refined as those of mineral seal and transformer oil quality have unsulfonated residues as low as 90 to 92%. Very considerable amounts of strong sulfuric acid or equivalent selective solvent agents are required in their preparation, treating yields are low, and large amounts of acid sludge or solvent extracts, etc., must be disposed of.

It has now been found that the summary classification of any and all unsaturated hydrocarbons as phytocidal, that is, as harmful or injurious to growing plant foliage, is erroneous, and that, while some types of unsaturated hydrocarbons may be and undoubtedly are phytocidal, at least one type is altogether harmless and therefore to be considered as safe for summer spray usage as are the most highly purified mineral oils of natural origin. In particular, it has been found that aliphatic mono-olefines, an acyclic class of unsaturated hydrocarbons characterized by the presence of one double, unsaturated or ethylene bond, may be used on growing plant foliage with a safety equal to that of petroleum oils of white oil grade, and that, moreover, these hydrocarbons of the aliphatic olefine type are insecticidal and fungicidal to a degree equal to or superior to those of the naturally occurring oils.

While it is not definitely understood why the unsaturated hydrocarbons must be so completely

removed from a naturally occurring oil or distillate before it can safely be used on foliage in the growing season, in view of the now discovered safety attending the use of unsaturated hydrocarbons of the aliphatic olefine type, it may be pointed out that in crude petroleums and their distillates there is a great variety of types of unsaturated and aromatic compounds, some of which are more or less easily polymerizable or oxidizable to resinous or asphaltic bodies and organic acids or oxygen-containing derivatives: it is at least possible, if not probable, that the polymerization or oxidation products of certain of these unsaturated and aromatic hydrocarbons are the actual agents harmful to plant foliage. However this may be, it has been found that the aliphatic olefines as a class do not polymerize or oxidize to give resinous or asphaltic bodies or harmful oxygen-containing derivatives in the manner characteristic of those naturally occurring petroleum oils which contain an appreciable proportion of "unsaturated hydrocarbons" or which have a low "unsulfonated residue". In any case, no harm results from their use as parasiticides on growing plant foliage.

It has been recognized that hydrocarbons of too low a viscosity are harmful to many types of growing foliage, by reason of their too great penetrability of growing plant tissues; furthermore, it has long been understood that the effectiveness of hydrocarbons as parasiticides increases as their viscosity increases, but it has also been understood that hydrocarbons of too low a volatility or vapor pressure are harmful to growing foliage in that they remain too long thereon subsequent to the completion of their utility as parasiticides. It has further long been understood that unsaturated hydrocarbons as a class are of higher parasiticial power than are saturated hydrocarbons, and unsaturated hydrocarbons or petroleum oils containing them would long since have been employed in horticultural spray compositions were it not for the phytocidal effects known to result upon application of petroleum spray oils of low unsulfonated residue. The aliphatic mono-olefines as a class provide a wider range of viscosities and a higher viscosity for a given volatility or boiling point range than do the hydrocarbons of natural petroleum origin when the latter are refined to usual spray oil quality and, inasmuch as they are entirely unsaturated, it will be evident that their application for parasiticial purposes is extraordinarily advantageous in that their high viscosity, high volatility and entirely unsaturated character combine in a single oil the ideal requirements of a parasiticide of this class, namely, high parasiticial effectiveness and low phytocidal propensities, as now ascertained.

The aliphatic olefine spray oils described herein, an acyclic class of hydrocarbons characterized by the presence of one double or unsaturated carbon to carbon bond, may be prepared in a variety of ways. They may be conveniently derived from any gaseous and/or low boiling point mono-olefines or from gaseous or liquid mixtures containing them, by—

(1) Polymerizing the low boiling point or gaseous olefines for the production of a series of liquid polymers of higher and often wide boiling point range, in the presence of a suitable polymerization catalyst;

(2) Separating by fractionation the produced higher boiling point olefinic polymers into frac-

tions of the desired viscosity or boiling point range.

Suitable olefine-containing gases or low boiling point liquids for the preparation of such olefine spray oils are those obtained in the pyrogenetic cracking of high boiling point petroleum oils for the production of motor fuels, as in the ordinary "cracking" processes. In exemplification of such methods of preparing satisfactory olefine spray oils:

Example 1.—A liquefied normally gaseous "cracked" petroleum distillate fraction, composed of about 80 volume percent of butane plus normal and iso-olefines, 14 volume percent of propane plus propylene, and smaller amounts of both lower and higher boiling hydrocarbons, was treated with sodium plumbite solution for the removal of hydrogen sulfide and mercaptans and was thereafter charged in increments to a reaction vessel where it was agitated with anhydrous aluminum chloride as a polymerization catalyst. The time required for substantially complete polymerization of the olefines was about one-half hour. During the polymerization reaction a considerable amount of heat was evolved; a reflux condenser connected to the reaction chamber was used to abstract this heat and control the temperature and pressure during the progress of the polymerization reaction, as well as to return olefine vapors for complete reaction. About 10 U. S. gallons of polymers were produced per pound of aluminum chloride used (about 83 liters polymers per kilogram aluminum chloride). An aluminum chloride tar and an oily liquid appeared as immiscible layers; the aluminum chloride tar was removed, and the mixture of olefine polymers and inert low boiling point saturated hydrocarbons was washed with water and charged to a still in which the low boiling point saturated hydrocarbons were vaporized. The olefine polymers thus produced had an initial boiling point of about 200° F. (about 93° C.) at atmospheric pressure and an end boiling point above 600° F. (above 315° C.) at a pressure of 10 millimeters of mercury. Upon fractionation of these polymers for the production of an olefine spray oil, about 47.5 volume percent of an oil was obtained which had a gravity of 37–38° A. P. I. (specific gravity 0.835–0.840 at 15.56° C.) and a boiling point range between 235° and 500° F. (between 113° and 260° C.) at 3.5 millimeters of mercury pressure. This oil had an unsulfonated residue of about 8%, an empirical formula C_nH_{2n} , and was composed of aliphatic mono-olefines, in the substantial absence of aromatic, cyclic or unsaturated hydrocarbons of other types.

Example 2.—A gas obtained in the thermal "cracking" of petroleum oil, all of whose constituents were gaseous at atmospheric temperature and pressure, containing about 27% of mono-olefines, was bubbled through a suspension of anhydrous aluminum chloride in petroleum ether at atmospheric temperature and pressure. An aluminum chloride tar and an oily liquid appeared as immiscible layers. These layers gradually increased in volume until, before the activity of the catalyst had appreciably diminished, about 8 gallons of polymers had been produced per pound of catalyst (about 67 liters polymers per kilogram of catalyst), exclusive of the petroleum ether originally present as carrier. The gaseous olefines were substantially completely polymerized. The petroleum ether originally present as carrier, together with the inert saturated hydro-

carbons present in the gaseous mixture charged, as absorption products, were separated from the olefinic polymers by vaporization, as in Example 1, and olefine spray oils of satisfactory volatility were obtained by fractional distillation.

When anhydrous aluminum chloride is used as polymerization catalyst, it has been found that the effect of polymerization temperature on the boiling point characteristics of the product formed is quite important. In the figure forming a part of this specification there are plotted the boiling point characteristics of the polymers that were formed from a mixture of normal and isobutenes, with anhydrous aluminum chloride as catalyst, at four different and controlled polymerization temperatures, namely, 60°, 125°, 150° and 200° F. (15.6°, 51.7°, 65.6° and 93.3° C., respectively). From the results there shown it will be observed that there is a definite increase in yield of lower boiling point polymers as the polymerization temperature is increased, and for this reason it is preferred that polymerization temperature be held slightly above atmospheric merely in order that greater yields of olefinic hydrocarbons may be obtained within the suitable spray oil range. Polymerization temperatures should not be allowed to go appreciably over about 350° F. (176.7° C.), however, for at such temperatures, when anhydrous aluminum chloride is the polymerizing agent used, decomposition of the polymers with the production of low boiling point hydrocarbons begins to be apparent.

In the tabulation below are presented the physical characteristics of two of the olefine oils found suitable for use as parasiticides, prepared in the manner described, in comparison with the physical characteristics of a highly refined "naphthene base" petroleum oil now in wide and highly acceptable use for the same purpose.

	Olefine spray oil No. 1		Olefine spray oil No. 2		100% unsulfonated residue naphthene base spray oil	
Distillation, at 3.5 mm. Hg pressure:	°F.	°C.	°F.	°C.	°F.	°C.
Start.....	235	112.8	300	148.9	220	104.4
5%.....	296	146.7	315	157.2	290	143.3
10%.....	310	154.4	323	161.7	306	152.2
20%.....	330	165.6	343	172.8	332	166.7
30%.....	340	171.1	361	182.8	345	173.9
40%.....	358	181.1	383	195.0	366	185.6
50%.....	371	188.3	400	204.4	377	191.7
60%.....	386	196.7	417	213.9	398	203.3
70%.....	401	205.0	439	226.1	407	208.3
80%.....	416	213.3	461	238.3	435	223.9
90%.....	441	227.2	491	255.0	470	243.3
98%.....					512	266.7
Gravity, °A. P. I.....	37.7		37.3		29.7	
Sp. gr. at 15.56° C.....	0.838		0.838		0.878	
Viscosity at 100° F. (37.8° C.):						
Universal Saybolt, secs.....	190		255		105	
Redwood, secs.....	161		216		90	
Engler No.....	5.63		7.50		3.16	
Unulfonated residue percent.....	8		8		100	

In the tabulation, unsulfonated residues of 8% are not necessarily indicative of the presence of saturated hydrocarbons: the substantial absence of saturated hydrocarbons in the olefinic oils is indicated by their bromine numbers and by their empirical formula C_nH_{2n} .

Olefine spray oils such as these have been found perfectly safe for application on growing plant foliage, even of the most delicate sort, under any of the conditions in which the most highly refined petroleum oils (for example, those of the "100% unsulfonated residue" type) have found adaptation. For example:

A group of lemon trees, in the flowering and fruiting season, was treated with the aliphatic olefine spray oil identified as "Olefine Spray Oil No. 2" in the tabulation above, in the form of a two percent emulsion in water, in the ordinary manner, with the addition of a small amount of a spreading and wetting agent. A second group of trees in the same grove was treated at the same time and under identical conditions with a two percent emulsion of the highly refined petroleum oil identified as "100% Unsulfonated Residue Naphthene Base Spray Oil" in the tabulation above. All of the trees treated were severely infested with California Red Scale and were moderately infested with Red Spider. After 60 days, mortality counts were made: On heavily infested fruits, mortality with the olefine oil was 97.1%; mortality with the 100% unsulfonated residue oil was 93.3%. On heavily infested twigs, mortality percentages were nearly identical for the two oils, 76.4% and 76.7%, respectively. The tree reactions in general, as regards leaf- and fruit-drop, were normal in all cases. Six months after the treatment, both groups of trees were again examined and were found normal in every respect.

As has been noted above, olefinic oils of any desirable or suitable viscosity and/or boiling point range may be obtained by fractionation of the olefine polymers first produced. As principally described hereinbefore, these olefine polymers are advantageously prepared by the use of anhydrous aluminum chloride as catalyst, but other polymerizing catalysts, such as anhydrous ferric chloride and boron trifluoride, may likewise be employed. Strong phosphoric acid, either as such or upon fusion with siliceous adsorbents, may also be employed as polymerizing catalyst when gaseous olefines are employed as initial materials; these catalysts produce polymers largely boiling below the usual spray oil range, however, with only lesser quantities of such viscosity and volatility as make them adaptable for parasiticide spray purposes. In all events, the initial olefine-containing materials should be substantially freed from sulfur-containing compounds and from such hydrocarbons as produce cyclic unsaturated or aromatic hydrocarbons upon polymerization or condensation; the polymerization catalysts and conditions of polymerization should likewise be chosen so that cyclic unsaturated and aromatic hydrocarbons are not formed, for, as has been pointed out, the acyclic olefine hydrocarbons characterized by the presence of one double carbon: carbon bond or linkage comprise the olefinic spray oils of this invention.

These olefines, of suitable spray oil viscosity and volatility, may likewise be prepared by the dehydration of the higher aliphatic saturated alcohols, followed by such polymerization of resulting olefine hydrocarbons as is sufficient to produce spray oils of the desired viscosity and volatility range.

Upon exposure to light and air in parasiticide service, these olefine spray oils, of spray oil viscosity and volatility, form far smaller quantities of phytocidal oxidation and polymerization products (that is, asphaltic bodies and asphaltogenic acids) than are formed upon similar exposure of highly treated petroleum spray oils. Attention has already been called to the very high viscosity of these olefine oils, as compared with the petroleum oils, for equivalent boiling point (volatility) range, and the significance of increased viscosity

together with high volatility in parasiticial oils has been noted above.

It should be noted that olefines with boiling points above about 600° F. (315° C.) at 3.5 millimeters of mercury pressure should not be present in the spray oils as applied to foliage; olefines boiling above that point should be segregated and discarded, as in the fractionation operation described, for it has been found that such high boiling olefines or polymer fractions have so low a vapor pressure and volatility as to remain too long on the foliage, detrimental to plant physiological processes and prejudicial to the appearance and cleanliness of fruit and foliage.

The olefinic spray oils here described may be blended or admixed with well refined petroleum-derived spray oils of the type now in wide and accepted parasiticial use, if desired, and such blends may be of advantage in particular instances where certain viscosity and volatility characteristics are sought, not easily obtained by the application of either type of spray oil alone; in such blending, the refined petroleum spray oil component should have an unsulfonated residue of at least 85%, for summer spray applications. Likewise, the olefine oils may be blended with more volatile, less viscous products either of the same type or of the type of well refined kerosenes, where wide coverage of insect and foliage with very thin ultimate films is desired: the lower cost of the more volatile diluents often makes possible more economical insect kills and avoids the application of thick films of viscous oil to sensitive plant foliage. In dilution of this sort, the olefine oils may be diluted with from one to as much as ten times their volume of the more volatile and less viscous oil, as desired.

In general, these olefinic spray oils are applied to the foliage harboring the insect or fungus pests in emulsified or in finely-divided mist or fog-like form, in operations found acceptable with the use of highly refined petroleum oils for the same purposes.

In applying the oils in unemulsified form, either as such or diluted with a less viscous oil-miscible diluent such as kerosene, it is preferable to employ a device which disperses the liquid in the form of droplets of sizes within the approximate range 0.07 to 0.30 millimeter in diameter, in an air stream of large volume and high velocity but of low pressure, directed into and around the foliage to be enveloped. Droplets of smaller diameter than 0.07 millimeter tend to float away and dissipate in the atmosphere, with consequent loss of oil and ineffectual contacting of parasites, while droplets of greater than 0.30 millimeter diameter tend to drench the foliage and the pests with an unnecessary amount of oil, wasteful and sometimes injurious to the vegetation. In the absence of devices capable of producing droplets largely within this preferable size range, these olefine oils may be applied as sprays in the manner common with petroleum sprays, observing the same precautions as are there understood.

For application to plant pests in emulsions in water, it is preferable to employ the olefine oils in concentrations of between 1 and 4%, but concentrated stock emulsions and "soluble oils" or "miscible oils" containing from 75-95% of oil may be prepared and stored, for later dilution with water at the time of parasiticial application. Thus alkali metal or lime "caseinate" with smaller amounts of soda or potash fatty acid soaps may be used in preparing stock emulsions, and the alkali metal soaps of either oil-soluble or

water-soluble sulfonic acids derived in the treatment of petroleum lubricating oil distillates with strong sulfuric acid, alcoholic potash phenol and rosin soaps, partially hydrolyzed esters of glycerol and higher fatty or naphthenic acids, and the like, may be employed in preparing mixtures which emulsify readily upon the addition of water, with agitation. In the employment of sodium soaps of petroleum sulfonic acids, for example, 2% thereof in olefine oil solution provides a ready emulsion in 50 times its volume of water. Likewise, oleic or similar fatty acids and fatty oils may be dissolved in the olefine spray oils, in small amounts, and emulsification in water brought about by addition of this mixture to a prepared water in which has been dissolved a caustic alkali or carbonate or even a neutral water-soluble soap.

The olefine spray oils are compatible with stomach poisons such as lead arsenate, Bordeaux mixture and lime-sulfur solutions; if such poisons are applied together with emulsions of the oils a suitable wetting and spreading agent or mixtures thereof will insure evenner and more effective distribution on the foliage: alkali caseinates, glue, gelatin, soap bark, dextrine, gamboge, blood albumen, water soluble sulfonic acids and molasses are suitable spreading and stabilizing agents for this purpose. These oils or emulsions thereof may likewise be employed in conjunction with nicotine extracts and with extracts or infusions of derris or cube, rotenone, pyrethrum and the like, in the amounts and in the manner in which they have been employed in conjunction with spray oils of the highly refined petroleum type spray oils.

While the character of the invention has been described in detail and numerous examples of its employment and application given; this has been done by way of illustration and with the intention that the invention shall not be limited thereto.

I claim:

1. A parasiticial oil consisting substantially entirely of liquid aliphatic mono-olefine hydrocarbons, the said olefine hydrocarbons boiling in major part above about 235° F. and below about 600° F. at 3.5 millimeters mercury pressure.

2. A parasiticial oil consisting substantially entirely of liquid aliphatic mono-olefine hydrocarbons boiling within the range 235° to 600° F. at 3.5 millimeters mercury pressure.

3. A parasiticial composition comprising liquid aliphatic mono-olefine hydrocarbons boiling in major part above about 235° F. and below about 600° F. at 3.5 millimeters mercury pressure, in the substantial absence of cyclic unsaturated and aromatic hydrocarbons.

4. A parasiticial composition comprising liquid aliphatic mono-olefine hydrocarbons boiling within the range 235° to 600° F. at 3.5 millimeters mercury pressure, in the substantial absence of cyclic unsaturated and aromatic hydrocarbons.

5. A non-phytotoxic parasiticial composition for application in liquid spray form to plant foliage comprising liquid aliphatic mono-olefine hydrocarbons boiling in major part above about 235° F. and below about 600° F. at 3.5 millimeters mercury pressure, in the substantial absence of cyclic unsaturated and aromatic hydrocarbons.

6. A non-phytotoxic parasiticial composition for application in liquid spray form to plant foliage comprising an admixture of liquid aliphatic mono-olefine hydrocarbons with from one to ten times their volume of a more volatile non-

phytotoxic hydrocarbon diluent, the said olefine hydrocarbons boiling in major part above about 235° F. and below about 600° F. at 3.5 millimeters mercury pressure.

5 7. A non-phytotoxic parasiticidal composition for application in liquid spray form to plant foliage comprising an admixture of liquid ali-
10 phatic mono-olefine hydrocarbons with an emul-
sifying agent, the said olefine hydrocarbons boil-
ing in major part above about 235° F. and below
about 600° F. at 3.5 millimeters mercury pressure.

15 8. A non-phytotoxic parasiticidal composition for application in liquid spray form to plant foliage comprising an admixture of liquid ali-
phatic mono-olefine hydrocarbons with a petrole-
um horticultural spray oil, the said olefine hydro-
carbons boiling in major part above about 235°
F. and below about 600° F. at 3.5 millimeters
mercury pressure and the said petroleum spray

oil having an unsulfonated residue of at least 85%.

9. A method of combatting plant parasites re-
siding on plant foliage comprising applying to the
foliage a non-phytotoxic liquid spray containing
5 liquid aliphatic mono-olefine hydrocarbons boil-
ing in major part above about 235° F. and below
about 600° F. at 3.5 millimeters mercury pressure,
in the substantial absence of cyclic unsaturated
and aromatic hydrocarbons.

10 10. A method of combatting plant parasites
residing on plant foliage comprising applying to
the foliage a non-phytotoxic liquid spray con-
taining liquid aliphatic mono-olefine hydrocar-
bons boiling within the range 235° to 600° F. at
15 3.5 millimeters mercury pressure, in the substan-
tial absence of cyclic unsaturated and aromatic
hydrocarbons.

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