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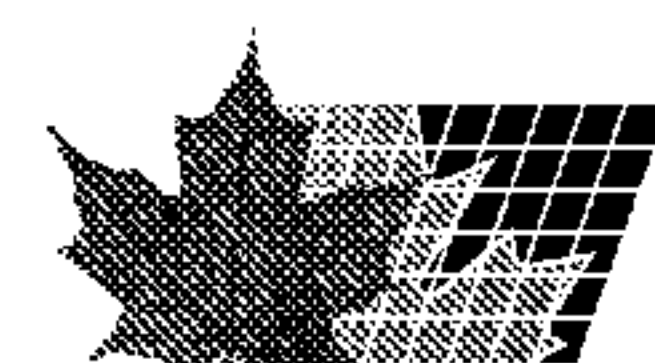
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(57) Abrégé/Abstract:

Active ingredient containing liquid formulations wherein the active ingredient is made water and oil resistant after application thereof to a substrate by the addition to the formulation of a fluorinated acrylic copolymer. The substrate can be either an animate or inanimate object. Active ingredients include repellents, attractants, pesticides, growth regulators, sunscreen agents, or medicines. The liquid formulations can be aqueous or organic solvent based or a mixture thereof.





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(54) Title: PROTECTIVE COMPOSITIONS

(57) Abstract

Active ingredient containing liquid formulations wherein the active ingredient is made water and oil resistant after application thereof to a substrate by the addition to the formulation of a fluorinated acrylic copolymer. The substrate can be either an animate or inanimate object. Active ingredients include repellents, attractants, pesticides, growth regulators, sunscreen agents, or medicines. The liquid formulations can be aqueous or organic solvent based or a mixture thereof.

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PROTECTIVE COMPOSITIONS

Background of the Invention

This invention relates to liquid compositions characterized by increased or extended efficacy of the active ingredient therein, even though the composition is exposed to water and/or oil after application thereof to a substrate.

Active ingredient formulations such as herbicidal or insecticidal formulations which utilize water are traditionally formulated with emulsifiers. These emulsifiers are surface active agents which remain with the active ingredient after the formulation has been applied to a substrate and dried. When water, e.g. rain, comes into contact with the applied formulation, it is subject to re-emulsification and ready removal or dilution of the active ingredient from the substrate. It is obvious that as the active ingredient is removed, in whole or in part, by water contact that the intended benefit of the active ingredient is eliminated or reduced. Thus, it is common on many product labels and inserts of active ingredient formulations such as herbicide formulations, insecticide formulations, sunscreen formulations, etc. to find a cautionary statement that if the formulation is contacted by or exposed to water within 2, 12, 24 or 48 hours, or the like, after application, then reduced efficacy or effectiveness can be expected and the formulation should be reapplied. Similarly, hydrophobic materials such as oils, fatty acids, sebum, etc. can solublize the active ingredient of formulations such as insect repellent and insecticide formulations as they come in contact with each other. Thus, the active ingredient can be removed, in whole or in part, from the substrate, thereby eliminating or reducing the effectiveness of the active ingredient. The present invention inhibits the removal of active ingredients from formulations by water or oil contact after application thereof to a substrate. This invention, therefore, eliminates or significantly reduces the need for re-application of active ingredient formulations.

Summary of the Invention

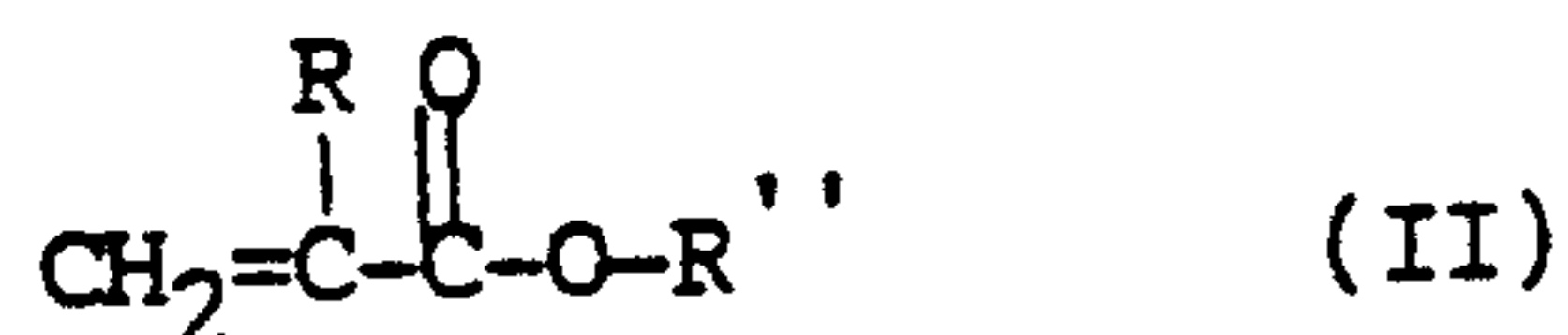
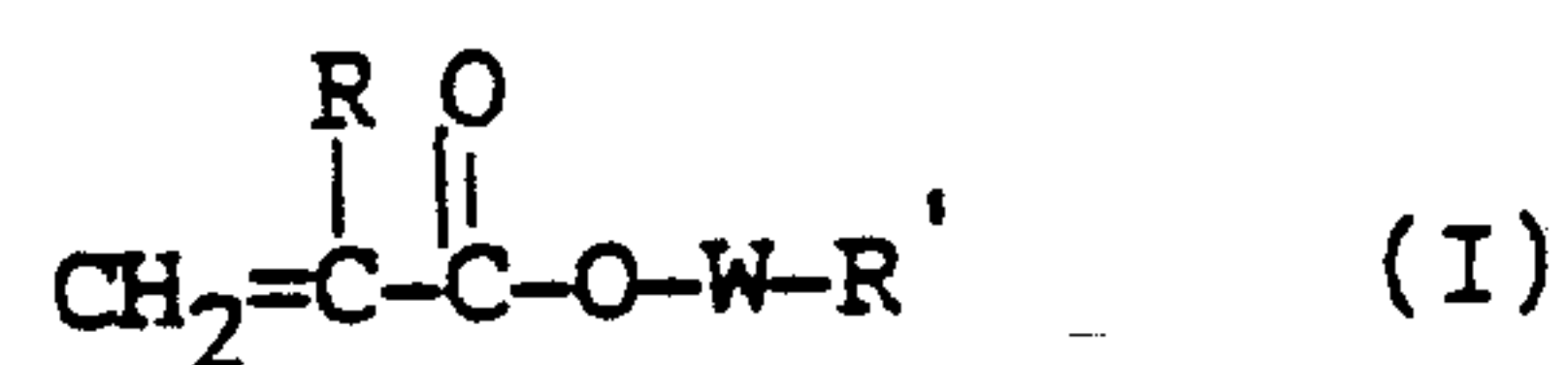
The present invention is directed at an active ingredient containing liquid formulation which contains a fluorinated acrylic copolymer in an amount effective to make the active ingredient(s) resistant to removal or dilution by water or oil after application

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thereof to a substrate. Fluorinated acrylic copolymers useful in the present invention are exemplified by the fluoroacrylic copolymers supplied by Atochem under the product name Foraperle such as Foraperle B208, 300 and 303.

5 The improved formulations of the present invention can be used on substrates such as humans, small and large animals, vegetation, hard surfaces traps, baits, etc. Active ingredients containing liquid formulations include formulations in which the active ingredient is a repellent, an attractant, a pesticide, a growth regulator, a sunscreen
10 agent, etc. The active ingredient liquid formulations of this invention can be water-based or organic solvent-based.

The fluorinated acrylic copolymers useful in the water and oil resistant formulations of the present invention include copolymers prepared by the polymerization of a perfluoroalkyl acrylate monomer of
15 formula I and an acrylate monomer of formula II:



20 wherein R is hydrogen or a lower alkyl of 1 to 4 carbon atoms, W is an alkylene of 1 to 6 carbon atoms, R' is a perfluoroalkyl of 2 to 20 carbon atoms and R'' is lower alkyl of 1 to 6 carbon atoms, hydroxyalkylene of 2 to 4 carbon atoms or the group $-(\text{CH}_2)_n-\text{NH}-\text{R}'''$ in which R''' is lower alkyl of 1 to 6 carbon
25 atoms or cycloalkyl and n is an integer of 2 to 4.

The term "alkyl" includes straight and branched chain alkyl groups.

The term "cycloalkyl" means a cycloalkyl hydrocarbon of 4 to 8 carbon atoms.

30 The fluorinated acrylic copolymers can be prepared by polymerization such as emulsion polymerization using standard procedures such as described in U.S. Patents No. 4,478,975 and 4,778,915. The copolymers are prepared using about 1 to 30 percent of a monomer of formula II, more usually 1 to 10 percent, based on the total weight of monomers I and II.

The amount of fluorinated acrylic copolymer included in an active ingredient liquid formulation to make the active ingredient, water and

oil resistant may vary from one formulation to the next. The most effective amount of fluorinated acrylic copolymer can be easily determined by routine testing. Generally, the fluorinated acrylic copolymer will be present in the liquid formulation within the range of about 1 to 20 percent by weight of the total formulation, more usually, 2 to 10 percent.

Detailed Description of the Invention

The following examples are provided to illustrate the practice of the present invention.

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Example 1

The following active ingredient liquid formulations (animal insect repellent spray) were prepared and tested on large long haired Labrador Retrievers.

	Formulation 1	
15	<u>Ingredients</u>	<u>Percentage</u>
	1. Water	89.008
	2. Carbopol 1342*	.150
	3. Ammonium Hydroxide 28%	.075
	4. Cypermethrin 90%	.167
20	5. Pyrethrins 20%	1.000
	6 Piperonyl Butoxide Tech.	1.600
	7. MKG 326**	.500
	8. MKG 11**	.500
	9. Stabilene** 100%	5.000
25	10. Foraperle 300***	2.0

* Crosslinked polymer of acrylic acid of B. F. Goodrich Co.

** Insect repellents of McLaughlin, Gormley King Co. and Union Carbide.

30

*** Fluorinated acrylic copolymer of Atochem, Inc.

Formulation 2 is the same as Formulation 1 with the exception that ingredient 10, the fluorinated copolymer, was omitted.

Formulation Procedure:

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1. Charge mixing vessel with ingredient 1 and adjust mixer until a vortex is created.
2. Sift ingredient 2 into vortex of ingredient 1. When ingredient 2 has been wet out, slow mixer to allow trapped air to escape and ingredient 2 to hydrolyze.
3. Add ingredient 3 and disperse completely.
4. Turn mixer up so as to pull a vortex, then add pre-blended ingredients 4 through 9 to make the emulsion. Reduce mixer speed but allow to mix until smooth.
5. Add ingredient 10 and mix until uniform.
6. Adjust pH to 6.0 $\pm$.2.

The practicality of and effectiveness of the animal insect repellent spray of Formulation 1 (in accordance with the present invention) was evaluated by treating two large long haired Labrador Retrievers with Formulation 1. The spray was applied to each animal's entire coat and allowed to dry.

Prior to treatment, the animals had extremely high mosquito counts (50-100) and they were penned in an environment with extremely high mosquito pressure.

To evaluate the water and oil proofing properties of Formulation 1, the animals were allowed to swim in a nearby creek every other day and were subjected to rain (sprinkling) on a frequent basis.

Observations were made each day with the following result. Formulation 1 was effective in maintaining the animals mosquito free for thirty days. The repellency started declining within the next five days and was ineffective by 35 days.

When the animals again had high counts of mosquitoes on their coat (50-100) they were sprayed with Formulation 2. The same procedure was followed for this evaluation as for the first. Formulation 2 was effective in maintaining the animals mosquito free for four days and was ineffective at the end of seven days.

Example 2

A premis spray was made and evaluated for water resistance as follows:

Formulation 3

Ingredients

1. DI Water

Percentage

93.275

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2.	Carbopol 1342	.150
3.	Ammonium Hydroxide	.075
4.	Permethrin	.500
5.	Piperonyl Butoxide	2.500
6.	Diazinon	.500
7.	Foraperle 303*	3.000

* Fluorinated acrylic copolymer of Atochem, Inc.

Formulation 4 was made the same as Formulation 3 except that ingredient 7 was omitted.

The same formulation or mixing procedure was used as in Example 1.

1. Six microscope slides were dipped into each of Formulation 3 and 4, allowed to dry 24 hours and weighed.
2. The slides were then placed identically under a stream of water with a steady flow and rinsed for 30, 90 and 300 seconds. The slides were then allowed to air dry for one hour.
3. Each slide was weighed and the amount of premis spray removed by rinsing calculated.

Results

20	<u>Formulation 3</u>	<u>Slide</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
	Treated Slide		4.52	4.36	4.37	4.41	4.37	4.44
	Untreated Slide		4.50	4.35	4.36	4.39	4.36	4.43
	Add On		.02	.01	.01	.02	.01	.01
	30 Sec. Rinse		4.52	4.36	4.37	--	--	--
25	Percent Loss		(0%)	(0%)	(0%)	--	--	--
	90 Sec. Rinse		--	--	--	4.41	4.37	4.44
	Percent Loss		--	--	--	(0%)	(0%)	(0%)
	300 Sec. Rinse		4.51	4.36	4.37			
	Percent Loss		(50%)	(0%)	(0%)			
30	<u>Formulation 4</u>	<u>Slide</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
	Treated Slide		4.48	4.46	4.47	4.48	4.51	4.48
	Untreated Slide		4.47	4.45	4.46	4.47	4.50	4.47
	Add On		.01	.01	.01	.01	.01	.01
	30 Sec. Rinse		4.47	4.45	4.46	--	--	--
35	Percent Loss		(100%)	(100%)	(100%)	--	--	--
	90 Sec. Rinse		--	--	--	4.47	4.50	4.47

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Percent Loss -- -- -- (100%)(100%)(100%

The fluorinated acrylic copolymer in Formulation 3 effectively increased the resistance of the premis spray to be rinsed from the slides by ten fold or more.

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Example 3

It is well known than an animal's body produces oils in the form of sebum which readily travel up the hair shafts found on the animal's body. These oils will act as diluents for the active ingredients and spread them over a larger surface area reducing their availability and dose levels. They also act as a release agent for the actives and allow them to be easily removed from the hair by the animal coming into contact with other substrates, such as the ground, bedding, etc.

The fluorinated acrylic copolymers used in the present invention when applied with active ingredients render them and the hair shaft hydro as well as lipophobic preventing the sebum from migrating up the hair shaft and diluting or displacing the active ingredients. To demonstrate this phenomena, the following comparison was made: A pyrethrin/PBO spray with and without a fluorinated acrylic copolymer was applied to three each beagles. The beagles were not bathed and were prevented from coming in contact with water other than drinking.

Formulation 5

	<u>Ingredients</u>	<u>Percentage</u>
	Isopropyl alcohol	30.00
	DI Water	44.58
25	Carbopol 1342	.15
	Ammonium Hydroxide	.03
	Pyrethrin 50%	2.00
	Piperonyl Butoxide	3.74
	Foraperle 303	19.50

30 The formulation was diluted at the ratio of 1 part Formulation 5 to 5.5 parts water prior to application to the animals.

Formulation 6 was the same as Formulation 5 except that Foroperle 303 was omitted. It also was diluted as above before application.

Results

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The total number of fleas and ticks found on three beagles which were infested with 100 fleas and 50 ticks 4 days pretreatment, and 2, 4, 8, 10, 13, and 20 days post treatment.

5	Days											
	Treatment	0	1	2	3	4	7	9	10	11	14	21
	Fleas											
	Formulation 5	83	0	0	0	0	0	5	3	24	13	16
	Formulation 6	85	5	0	1	0	5	34	27	87	75	—
10	Untreated	71	53	97	89	87	132	93	75	111	72	63
	Ticks											
	Formulation 5	34	11	0	0	0	1	5	5	42	34	38
	Formulation 6	50	25	7	14	7	37	29	28	76	71	—
	Untreated	42	41	39	56	54	67	65	64	87	82	54

Example 4

15 A sunscreen formula with and without a fluorinated acrylic copolymer was made and tested along with a commercially available waterproof sunscreen known as Bull Frog by Chattem, Inc. Each formulation was applied to strips of blotter paper and allowed to dry overnight. Drops of water were applied to each paper. The commercial
20 product (Bull Frog) as well as the formula without the fluorinated acrylic copolymer absorbed the water whereas the formula with the fluorinated acrylic copolymer (Foraperle 303) stood the water up in droplets and did not allow it to penetrate the paper.

The formulas were as follows:		<u>Percentages</u>	
25	DIH ₂ O	77.85	80.85
	Carbopol 1342	.5	.5
	Octyl Methoxycinnamate	7.5	7.5
	Oxybenzone	6.0	6.0
	Octyl Salicylate	5.0	5.0
30	TEA (Triethanol amine)	.15	.15
	Foraperle 303	3.00	----

Example 5

The following Formulation 7 was made and tested on large animals as a pour-on.

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Formulation 7

5	<u>Ingredients</u>		<u>Percentage</u>
	Isopropyl alcohol		30.00
	DI Water		65.82
	Carbopol 1342		.15
	Ammonium Hydroxide		.03
	Permethrin		1.00
	Foraperle 303		3.00

10 Formulation 7 was compared with a one percent permethrin pour on product known as DeLice by Durvet, Inc. which does not contain any fluorinated acrylic copolymer (Formulation 8). Three ounces of each formulation were applied to five head of cattle each. The following data show the average number of horn flies found on the cattle and the percent reduction corrected using Abbotts Formula (control minus 15 treatment divided by control times 100).

The Average Number of Horn Flies Found on
5 Head of Cattle

Days		Formulation 8	Formulation 7	Untreated Controls
20	0	840.0	940.0	800
	1	3.0	4.5	815
	7	6.5	6.0	920
	14	7.5	3.5	850
	21	25.5	2.5	1020
25	28	225.0	65.0	1275
	35	150.0	10.0	750

Percent Reduction Using Abbotts Formula

30	1	99.6	99.4
	7	99.2	99.3
	14	99.1	99.5
	21	97.5	99.7
	28	82.3	94.9
	35	66.6	97.7

Example 6

The following formulation is useful as a rose bush fungicide spray.

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	<u>Ingredients</u>	<u>Percentage</u>
	DI Water	97.846
	Pemulen TRI	.100
	Triethanol amine	.050
5	Triforine	.007
	Foraperle 303	2.000

The formulation extends the efficacy of the fungicide by extending the intervals between sprayings as compared to a formulation without the water proofing agent (fluorinated acrylic copolymer). It also prevents wash off and dilution of the fungicide.

Example 7

A herbicide spray concentrate was prepared as follows.

	<u>Ingredients</u>	<u>Percentage</u>
	Water	95.5
15	Pemulen TRI	.5
	Isopropylamine salt of glyphosate	2.0
	Foraperle 303	2.0

The concentrate is diluted with water before application to weeds. The presence of the fluorinated acrylic copolymer eliminates the need to retreat or reapply the herbicide formulation should it unexpectedly rain within about 6 to 24 hours from the time of applying the herbicide.

Example 8

Premis insecticidal sprays A and B, which resist water and oil were formulated as follows.

	<u>Ingredients</u>	<u>Percentage</u>
	A. Water	96.30
	Permulen TR2	.15
	Triethanol amine	.05
30	Resmethrin	.50
	Foraperle 303	3.00
	B, Mineral spirits	89.94
	Deltamethrin	.06

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Foraperle B208

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10.00

The fluorinated acrylic copolymer (Foraperle) makes formulations A and B both hydrophobic and lipophobic. The above formulations when applied to various substrates such as wood, tile, concrete, carpet, linoleum and the like not only resist wash off and dilution of the active ingredient by water but also resist dilution of the active ingredient and its being rendered unavailable due to absorption in various oils and greases found in restaurants, kitchens, and the like.

Without any intention of being bound by theory, it is believed that the active ingredients in the several formulations described herein are made water and oil resistant by the fluorinated acrylic copolymers when applied to a substrate for the following reason. Due to the general insolubility of the fluorinated acrylic copolymer and its low surface tension, when it is exhausted from the formulation along with the active ingredient to a substrate, the fluorinated acrylic copolymer coalesces and covers or disperses with the active ingredient rendering it water and oil resistant. In accordance with the present invention, the time span over which the active ingredient is effective is lengthened even though the active ingredient after being applied to a target substrate is adversely and/or prematurely contacted with water or oil. These properties are very important economically and environmentally because it eliminates or very significantly reduces the need for re-application of the active ingredient and lengthens the time between applications of the active ingredient.

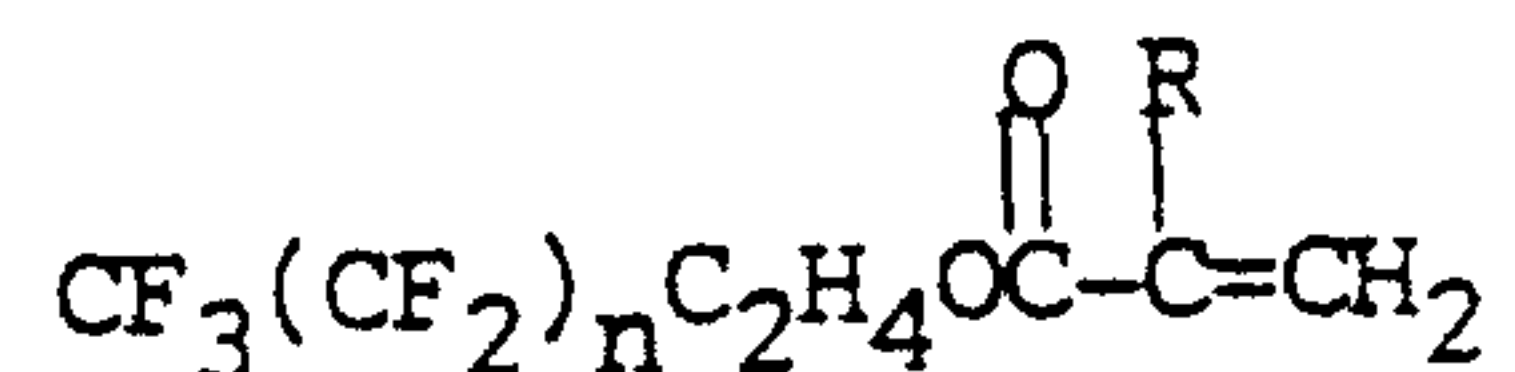
The addition of an effective amount of a fluorinated acrylic copolymer to any active ingredient containing liquid formulation imparts water and oil resistance to the active ingredient when it is applied to a substrate. The active ingredients of particular interest in liquid formulations include: insect and animal repellents; insect and animal attractants; insect and plant growth regulators; pesticides including insecticides, acaricides, parasiticides, herbicides and rodenticides; sunscreen agents; and medicines or pharmaceuticals for topical application. Specific examples within the foregoing active ingredients include: Stabilene, MGK 874, deet, MGK 326 and MGK 11; muscalure, disparlure, and trimedlure; glyphosine, norflurazon, methoprene, hyproprene and diflubenzuron; natural and synthetic pyrethroids, carbamates, organophosphates, triforine, glyphosate, methazole, warfarin and bromethalin; and anti-inflammatory agents.

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Among the fluorinated acrylic copolymers useful as the water and oil proofing agents in the present invention are those prepared by the polymerization of a perfluoroalkyl acrylate of formula I and an acrylate of formula II using conventional procedures. Perfluoroalkyl acrylate
5 monomers such as those of the formula



in which R is hydrogen or methyl and n is the positive integer 3 to 13 and mixtures thereof can be used to form a copolymer with an acrylate
10 monomer II such as ethyl methacrylate, methyl methacrylate, ethyl acrylate, 2-hydroxyethyl methacrylate, and mixtures thereof. Additional suitable acrylic monomers for the fluorinated acrylic copolymers used in the present invention are described in U.S. Patents No. 4,478,975 and 4,778,915.

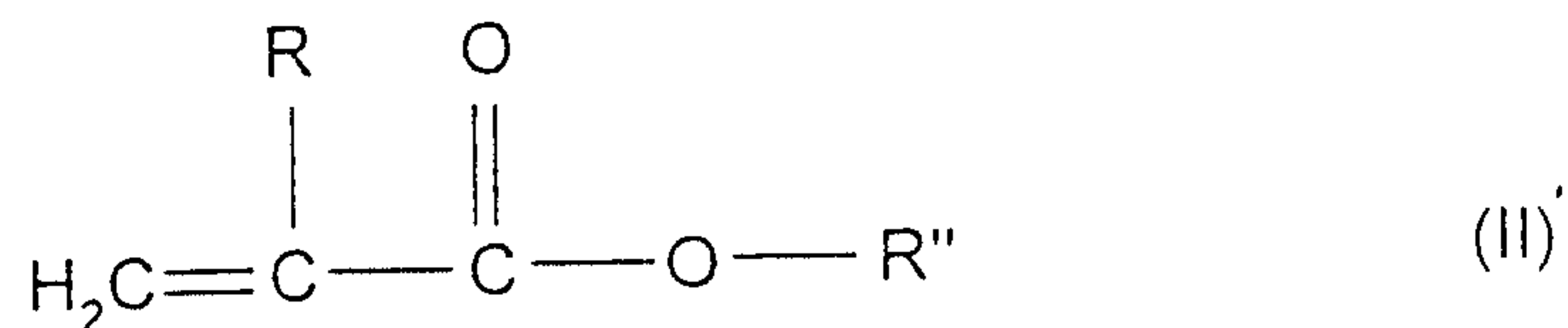
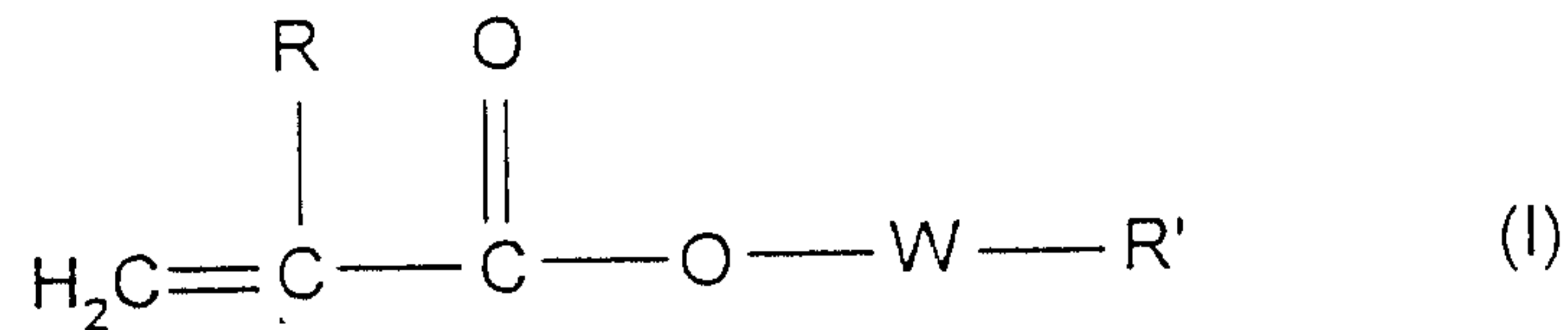
15 The term "substrate", as used herein, is used broadly to include both animate and inanimate objects. Thus, it includes humans, large animals such as cows and horses, small animals such as dogs, cats, swine and sheep, vegetation of all types, surfaces such as wood, concrete, metal, tile, textiles, plastic, etc.
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What Is Claimed Is:

1. An active ingredient-containing liquid formulation to be applied to a substrate, which liquid formulation is aqueous-based, organic solvent-based, or a combination thereof, and which liquid formulation comprises:
 - an effective amount of an active ingredient selected from the group consisting of insect repellents, insect attractants, animal repellents, animal attractants, insect growth regulators, plant growth regulators, sunscreen agents, anti-inflammatory agents, and pesticides selected from the group consisting of insecticides, acaricides, parasiticides, rodenticides, and herbicides; and
 - a fluorinated acrylic copolymer in a concentration effective to increase the resistance of the active ingredient to removal or dilution by water or oil after application of the liquid formulation to said substrate.
2. The liquid formulation of claim 1, wherein the fluorinated acrylic copolymer is present in the liquid formulation within the range of about 1 to about 20% by weight.
3. The liquid formulation of claim 1, wherein the active ingredient is an insect repellent.
4. The liquid formulation of claim 1, wherein the active ingredient is a sunscreen agent.
5. The liquid formulation of claim 1, wherein the active ingredient is a pesticide.
6. The liquid formulation of claim 5, wherein the pesticide is an insecticide.
7. The liquid formulation of claim 5, wherein the pesticide is an herbicide.

8. The liquid formulation of any of claims 1 to 7, wherein the fluorinated acrylic copolymer is formed from a fluorinated monomer of formula I and a monomer of formula II, said monomer of formula II being present in the amount of about 1 to 30 % by weight of the total weight of the monomers of formula I and II,



wherein R is hydrogen or a lower alkyl of 1 to 4 carbon atoms, W is an alkylene of 1 to 6 carbon atoms, R' is a perfluoroalkyl of 2 to 20 carbon atoms, and R'' is a lower alkyl of 1 to 6 carbon atoms, a hydroxyalkyl of 2 to 4 carbon atoms, or the group $-(\text{CH}_2)_n-\text{NH}-\text{R}'''$ in which R''' is a lower alkyl of 1 to 6 carbon atoms or a cycloalkyl, and n is an integer of 2 to 4.

9. The liquid formulation of claim 8, wherein the copolymer is formed by emulsion polymerization.

10. The liquid formulation of claim 8, wherein the monomer of formula II is present in the amount of 5 to 25 percent.

11. The liquid formulation of claim 8, wherein R is hydrogen or methyl, W is an alkylene of 2 to 4 carbon atoms, R' is a perfluoroalkyl of 5 to 12 carbon atoms, and R'' is a lower alkyl.

12. The liquid formulation of claim 8, wherein R is methyl, W is an alkylene of 2 carbon atoms, R' is a perfluoroalkyl of 5 carbon atoms, and R'' is methyl or ethyl.

13. Use of an active ingredient in a liquid formulation as defined in claim 1, the active ingredient being selected from the group consisting of insect repellents, insect attractants, animal repellents, animal attractants, insect growth regulators, plant growth regulators, sunscreen agents, anti-inflammatory agents and pesticides selected from the group consisting of insecticides, acaricides, parasitocides, rodenticides and herbicides for prolonging the effectiveness of an active ingredient to be applied to the surface of a substrate.
14. The use of claim 13, wherein the substrate is an animal.
15. The use of claim 13, wherein the substrate is a human.