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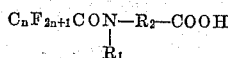
3,351,643

COORDINATION COMPLEXES

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 No Drawing. Filed Aug. 9, 1965, Ser. No. 478,408
 7 Claims. (Cl. 260-404)

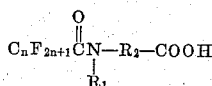
ABSTRACT OF THE DISCLOSURE

Chromium coordination complexes of compounds of structure



where $\text{C}_n\text{F}_{2n+1}$ is perfluoroalkyl, n is 8 to 12, R_1 is H or alkyl of 1 to 4 carbon atoms and R_2 is alkylene of 1 to 6 carbon atoms. The complexes are useful as water and oil repellents for felt, glass, paper, textiles, glass fibers, wood, metals, etc.

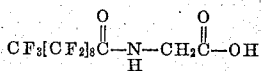
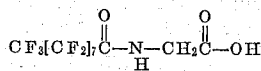
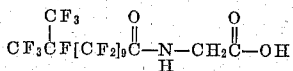
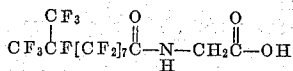
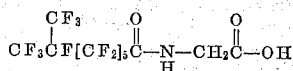
This invention is concerned with chromium coordination complexes of compounds of the general formula



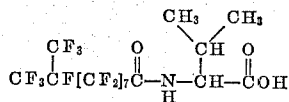
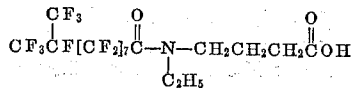
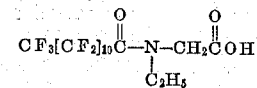
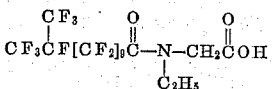
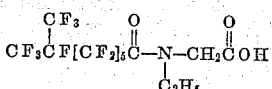
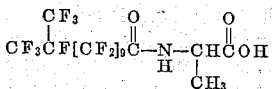
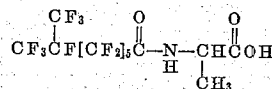
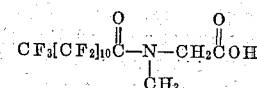
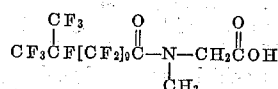
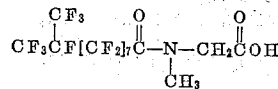
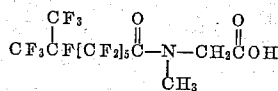
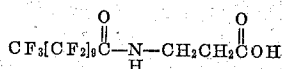
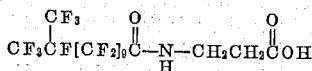
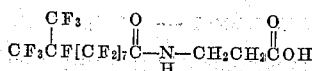
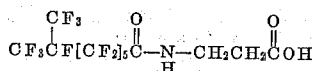
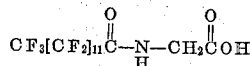
where $\text{C}_n\text{F}_{2n+1}$ is a perfluoroalkyl group which may have a straight or branched chain, n is an integer of from 8 to 12; R_1 is hydrogen or alkyl group (which may be straight or branched) having from 1 to 4 carbon atoms; and R_2 is an alkylene radical (which may be straight or branched chain) having from 1 to 6 carbon atoms.

Of particular value are the chromium complexes of compounds of the above type where the perfluoroalkyl group $\text{C}_n\text{F}_{2n+1}$ contains from 10 to 12 carbon atoms. Of particular value also are compounds of the above type where R_1 is hydrogen or an alkyl group containing from 1 to 2 carbon atoms; and those in which R_2 is an alkylene radical having from 1 to 3 carbon atoms.

Typical examples of the amido-acid compounds from which the chrome complexes of the invention may be made are shown in the form of the free acid as follows:



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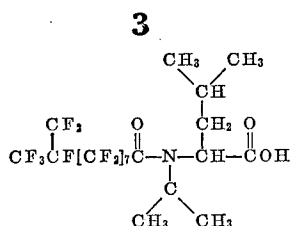
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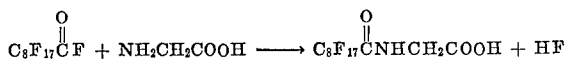
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The above compounds may be prepared by the direct reaction of the acid fluoride or the acid chloride of a perfluorinated carboxylic acid of the proper chain length with an amino acid. This reaction may be illustrated by the reaction of perfluorononanoic acid fluoride with glycine in accordance with the following:



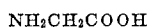
The reaction is preferably carried out by dissolving or suspending the perfluoro acid fluoride in an anhydrous solvent and mixing the solution slowly with a suspension of the amino acid in the same solvent and then heating or refluxing the mixture for several hours. The amino acid may be added slowly to the perfluoro acid fluoride or conversely, the acid fluoride may be added slowly to the amino acid. The reaction mixture is filtered to remove insoluble material which generally includes excess amino acid and its hydrogen fluoride salt, after which the amide product may be isolated by evaporation of the solvent and purified if necessary by crystallization, or similar techniques. Suitable anhydrous solvents include e.g. ethyl acetate, diethylether, dimethoxyethane,



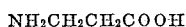
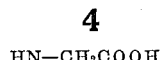
tetrahydrofuran, trichlorotrifluoroethane and benzene. Reaction temperatures of from 0° C. to 150° C. and more usually from 20° C. to 100° C. will generally be used. Sufficient amino acid is employed to insure high conversions of the perfluoro acid fluoride, molar ratios of the amino acid to the perfluoro acid fluoride of from 1:1 to about 3:1 being generally preferred. Reaction may be generally carried out most conveniently at atmospheric pressure and reaction times of from about 10 minutes to 10 hours are generally satisfactory. Further details on the preparation of these compounds will be found in the application of Hauptschein and Toukan, U.S. Ser. No. 276,160, filed Apr. 29, 1963, now U.S. 3,238,235.

The perfluorinated carboxylic acid fluorides used to prepare the compounds of the invention may be obtained in a variety of ways. Perfluorinated acid fluorides containing up to 10 carbon atoms may be prepared by the electrochemical fluorination of the corresponding hydrocarbon carboxylic acid in liquid hydrogen fluoride as described for example in U.S. Patent 2,519,983 of Simons. The perfluorinated acid fluorides may also be obtained by the reaction of perfluorinated iodides with fuming sulfuric acid as described in co-pending application Ser. No. 316,424, filed Oct. 15, 1963, of Murray Hauptschein and Chester L. Parris for Preparation of Fluorinated Organic Compounds. The fluorinated iodide precursors may be prepared by telomerization procedures such as by the reaction of perfluoroisopropyl iodide $(\text{CF}_3)_2\text{CFI}$ or perfluoroethyl iodide $\text{CF}_3\text{CF}_2\text{I}$ with tetrafluoroethylene to produce telomers of the formula $(\text{CF}_3)_2\text{CF}[\text{CF}_2\text{CF}_2]_n\text{I}$ and $\text{CF}_3\text{CF}_2[\text{CF}_2\text{CF}_2]_n\text{I}$ respectively.

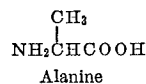
Examples of suitable amino acids useful for preparing the above amido-acid compounds are the following:



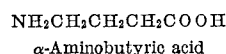
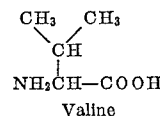
Glycine

 β -Alanine

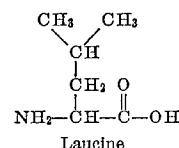
Sarcosine



Alanine

 α -Aminobutyric acid

Valine



Laucine

The chrome complexes are made from the above compounds by methods similar to those described in the prior art; see for example, Example 1 of U.S. 2,934,450; Example 4 of U.S. 2,273,040 and Example V of U.S. 2,544,666. In a general preferred procedure for preparing the complex, a solution of chromic chloride in an alcohol (e.g. methanol, isopropanol, etc.) is first prepared and heated to 50° C. A solution of sodium hydroxide in methanol is then added dropwise with agitation to the alcoholic chromic chloride solution. After the addition is completed, the mixture is refluxed and the desired fluorocarbon amido-acid is then added after which refluxing is again carried out. After cooling to room temperature the reaction product is filtered and adjusted with alcohol to the desired solids content.

In the preferred procedure methyl alcohol or isopropyl alcohol will be used as a solvent and instead of using a single fluorocarbon amide-acid, a mixture of such acids will be used, preferably a mixture of acids containing 11 and 13 carbon atoms in a fluorocarbon acid portion of the molecule. The weight ratio of the preferred acid mixture is such that the ratio of 11 carbon acid to 13 carbon acid is preferably 3 to 2 or higher. In adjusting the reaction product to a specific solids content, the preferred solids content will be on the order of about 30% by weight.

One of the advantages of the chrome complexes of the invention is that the product may be prepared and used with a wide molar ratio of chromium to fluorine containing compounds. Since the fluorine containing compounds are the most expensive ingredient in the final composition, it follows that the cost can be reduced significantly if a large molar ratio of chromium to fluorine containing compound may be used. It has been found that molar ratios as high as 50:1 can effectively be used in order to obtain compounds which exhibit water and oil repellent properties. However, the ratio preferably employed will be in the order of 2:1 to 15:1. The chromium complexes prepared by the above procedures may be isolated as green colored solids, but preferably the compounds are used directly in the aqueous alcoholic solutions in which they are prepared. These solutions will generally have a concentration of chrome complex at time of preparation of between about 30 and 40% by weight, and are ready for use simply by diluting with water to the desired use concentration. It is preferred to sell the product concentrate obtained in the preparation and supply users with a concentrated aqueous alcoholic solution, which as noted above is simply diluted for use.

Preferably, the users will be supplied with an alcohol solution containing 25 to 35% by weight of the chrome complex. The user generally will dilute such concentrates

with water so that the resulting solution will contain 0.05 to 3.0% by weight of the complex. It will be understood, however, that higher and lower concentrations may be used.

The alcoholic concentrate which, as described above is diluted with water for use, is a green solution which is stable to storage until ready for use. Upon dilution with water, the diluted product should be used within 24 hours to avoid any changes in composition which may occur due to further oxidation and oxolation of the chromium complex with water. Typical analysis for the green, alcoholic concentrate is as follows:

Molar Ratio of chromium: fluoro acid: caustic	Solvent	Percent by weight			
		Cr	Cl	F	H ₂ O
6:1:2.7	Isopropanol.....	5.7	9.0	7.3	10.8
6:1:2.7	Methanol.....	6.0	10.1	7.5	12.2
3:1:1.9	Isopropanol.....	4.4	6.7	12.4	7.6

The chrome complexes of the invention may be used in a wide variety of applications in order to make surfaces such as cellulose films, paper, wood, leather, textile fibers, yarns, fabrics, glass, ceramic products, metals, etc., water and oil repellent, while not significantly affecting properties such as flexibility, hand, etc.

The methods of using the compounds of the invention for imparting water and oil repellent properties to various substrates are those conventional procedures used in the trade with other agents. When treating leather, for example, the agents will be drummed into tanned skins to give an internal treatment and in some applications may be sprayed on leather surfaces to give a top coat. In other types of leather treating application, the compounds of the invention will be used to give an internal treatment and a top coat will be applied by spraying the leather with a different material, as for example a fluorinated polyurethane resin. In their application to paper, the complexes will preferably be added to a paper size press in the paper mill. In other applications, spraying, padding, or other conventional techniques may be used.

Example 1.—Preparation of chrome complex

An apparatus was set up consisting of a 22 liter flask equipped with reflux condenser, mechanical stirrer and additional funnel. A solution of chromic chloride in methyl alcohol was prepared by dissolving 5437 grams of chromic chloride hexahydrate in 4240 grams of methyl alcohol while subjecting the liquid to moderate heat and stirring. Then 952 grams of sodium hydroxide was dissolved in 3200 grams of methanol at about 50° and the solution was added dropwise over a one hour period to the chromic chloride solution.

It is important that when the sodium hydroxide solution is added to the chromic chloride solution that it be added slowly and with strong agitation to avoid local high pH values which might precipitate basic chromic chloride or chromic hydroxide. The solution was then refluxed for one hour and a mixture of 1348 grams of $(CF_3)_2CF(CF_2)_7CONHCH_2COOH$ and 899 grams of $(CF_3)_2CF(CF_2)_9CONHCH_2COOH$ was added and the mixture again refluxed for another hour. The reaction mixture was then cooled to room temperature, filtered and adjusted to 30% solid concentration by the addition of methanol.

The chromium complex prepared in this manner corresponds to a molar ratio of chromium to fluorocarbon-amido acid of 6:1 and the molar ratio of fluorocarbon-amido acid to sodium hydroxide is 1:7.

Using the above general procedure, the following chrome complexes were prepared:

Fluorochemical composition of structure $(CF_3)_2CF(CF_2)_nCONHCH_2COOH$	Mole ratio	
	Cr:fluoroacid:	NaOH
n=5	6:1:7	
n=7	6:1:7	
n=9	6:1:7	
n=9	6:1:2.7	
n=7	6:1:2.7	
n=5	6:1:2.7	
Two component mixtures containing compounds where n=7 and n=9		
Ratio of components (n=7 to n=9)		
3:2	3:1:4	
3:2	6:1:2.7	
3:2	3:1:1.9	
3:2	6:1:4.4	
3:2	6:1:10	
3:2	6:1:7	
3:2	15:1:5	
3:2	30:1:9.6	
2:1	6:1:7	
2:1	6:1:2.7	
2:1	3:1:1.9	

Evaluation of products.—The products of the invention were evaluated in numerous tests to show the water and oil repellency and other properties which they impart to various surfaces. The test methods used were as follows:

(A) WATER RESISTANCE ON LEATHER

(1) *Water repellency.*—A.A.T.C.C. Method 22-1964.

(2) *Static water absorption.*—Leather samples are cut 2" x 2" weighed and hung in a beaker of water so that the upper edge is one inch below the water surface. The specimen is held below the surface and the same is removed at the end of one hour immersion. Surface water is then lightly blotted away and the sample reweighed to determine percent water absorbed. No allowance is made for water solubles.

(B) OIL RESISTANCE ON LEATHER

(1) *Surface oil repellency.*—This test consist of placing drops of mixtures of a mineral oil (Nujol) and n-heptane on the surface and noting the composition containing the highest percentage of n-heptane which does not wet the surface under the drop. The rating corresponding to that composition is considered the oil repellency of the sample.

Oil repellency rating scale

Oil repellency rating:	Percent n-heptane in mineral oil-heptane mixture (by volume)
150	100
140	90
130	80
120	70
110	60
100	50
90	40
80	30
70	20
60	10
50	0
0	(no holdout to Nujol)

(2) *Static oil absorption test.*—This test was designed to measure the degree of resistance of treated leather to absorption of oil under static conditions. A 2" x 2" specimen is weighed and hung upright in a beaker of pure mineral oil (Nujol) so that the upper edge is ¼" below the oil surface. After 10 minutes immersion the specimen is removed, surface oil lightly blotted off with absorbent paper, and reweighed to determine percent oil absorbed.

(C) CHEMICAL RESISTANCE ON LEATHER

Acid curl test

This is a test to measure the chemical resistance of leather exposed to acids. The curl test may be defined as the degree of curl exhibited by a strip of leather under acid attack, as measured by the angle of rise of the strip from a lateral surface in a specific period of time.

A sample of leather four inches by one-half inch is placed on a smooth, horizontal plane, and weighted down

lowed to dry for 2 minutes at 200° F. The strips are then tested for water and oil repellency in accordance with the above described surface repellency tests.

Test results

Effect on cotton cloth.—Compositions prepared in the manner described in Example 1, but at various chrome to fluorocarbon-amido ratios were evaluated on cotton cloth at various concentrations for oil and water resistance. The following Table I indicates the results obtained:

TABLE I

Oil and water repellency on cotton cloth of chrome complexes of a mixture of 2 parts (CF₃)₂CF(CF₂)₂CONHCH₂COOH and 3 parts (CF₃)₂CF(CF₂)₇CONHCH₂COOH at various chrome levels

	Percent Solids on Cloth Cotton											
	4		3		2		1		0.5		0.25	
	Repellency Ratings											
	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water
Molar Ratio of chromium to fluorocarbon-amido-acid:												
6:1.....	100	100	100	100	100	100	90	90	80	90	80	80
15:1.....	100	90	90	100	70	90	70	100	80	90	70	90
30:1.....	80	70	70	70	50	70	0	70	0	50	0	50
50:1.....	60	50	0	50	0	50	0	50	0	50	0	50
See note.....	90	80	90	80	90	80	70	80	60	80	0	80

NOTE.—Test sample was a chromium complex of C₈F₁₇SO₂N—CH₂—COOH having a chromium acid molar ratio of 3:1.
C₂H₅

at one end with a weight which covers approximately one inch of the sample. On the exposed three inches of leather, a surface area of one-eighth inch by one-half inch is covered with 37% hydrochloric acid applied across the sample one and one-half inches from the end. The angle of rise noted on the free end of the leather is measured at the end of five minutes.

Hot caustic resistance test

This method is designed to measure the resistance to penetration of hot caustic in treated leathers. 10 molar NaOH (40%) solution is heated to 100° C. Five drops of the hot solution are placed on the leather surface and allowed to remain for 5 minutes. After the leather is rinsed and dried, the affected area is observed for degree of burn and reported as: No effect, slight stain, slight burn, severe burn, or hole.

(D) OIL PENETRATION TEST ON PAPER

The chrome complex concentrate (30% solids) is diluted with water to the desired concentration for the selected wet pick-up. The solution will contain dissolved urea (to neutralize evolved HCl) and optionally, a non-ionic type surfactant. The paper sample is then treated with the prepared solution on one or both sides as desired using conventional application methods and the treated sample is cured at 120–130° C. for 5 minutes. The concentration of the diluted chrome complex solution may be varied to give different solids loadings.

The treated paper is then tested on the treated side by exposing it to various oils and noting the time for 50% penetration.

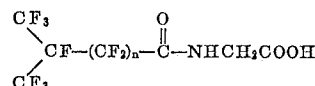
(E) OIL AND WATER REPELLENCY TEST ON COTTON CLOTH

Standard 9" x 9" test panels of standard 80 x 80 cotton cloth (4 oz. print cloth free of dyes, bleaches, and sizes) are used to pad onto the cloth a solution of the desired percent solids. The strips are then passed through a pressure rolls set to allow 100% pick-up of the solution and are placed on a rack and then put into an oven for a dry-cure at 350° F. for 3.5 minutes. At the end of the curing period, the strips are rinsed in water and then al-

The above table indicates the excellent repellent effects obtainable with the compounds of the invention and also indicates their superiority over chrome complexes of fluorocarbon sulfonamide type compounds. The higher the chrome to acid ratio, the less effect one obtains but it is seen that even at a ratio of 6:1 for the compounds of this invention the repellent effects are greater than for the sulfonamide type at 3:1. Table I-A which follows shows the oil repellency effects of chrome complexes where C_nF_{2n+1} ranges from C₈F₁₇ to C₁₂F₂₅ and it is seen that the oil repellency effect imparted by the compounds is excellent.

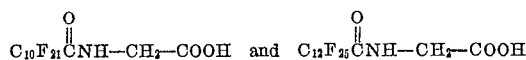
TABLE I-A

Oil repellency on cotton cloth of a 3.5:1 chromium complex of—



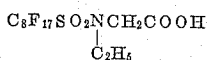
Cloth loading, Percent by weight	Oil Repellency		
	n=5	n=7	n=9
4	100	100	120
3	100	100	110
2	90	100	100

Effect on leather.—Twenty-five pounds of pigskins (blue shaved "crusts") were processed through a standard chrome tanning procedure, including application of syntan, dyeing, and fat liquoring and then placed in a wooden drum. Then 3.5 gallons of water at 115° F. were added and the drum was rotated for 15 minutes (pH of skins 3.5). At this point, 1.13 pounds of a 6:1 chrome complex of a 3:2 mixture of



was added which corresponded to 4.5% of the weight of the wet skins. The drum was rotated for 50 minutes with water at 100° F. and the skins then hosed for 3 hours and toggle dried. The treated skins exhibited excellent water and oil repellency, showed no acid curl nor any effect from hot caustic. Stain resistance and dry soil resistance was also excellent.

In a similar leather treatment procedure except that the internally treated skins were paste dried for 5½ hours at 150° F. staked, buffed, dry milled in a drum for 90 minutes and then top sprayed with a fluorinated polyurethane resin. Evaluation of the treated leather gave the data in the following table which also shows the test results when the same leather was treated in the same way except that the internal treatment was made with a 3:1 chrome complex fluorocarbon repellent made from a sulfonamide having the structure



Test	Rating	
	Chrome Complex of—	
	Fluorocarbon acid-amide	Fluorocarbon sulfonamide
AAATCC Spray.....	80	80
Oil repellency.....	100	80
HCl curl.....	0	0
Hot NaOH.....	No effect	No effect
Percent water absorption.....	52 to 68	74 to 84
Percent oil absorption.....	6 to 10	48 to 63

It is quite evident from the above table that the fluorocarbon acid-amide of the invention imparts excellent characteristics to leather treated with it. Of further significance, however, is the unexpected superior performance in water absorption and oil absorption properties as compared to the sulfonamide type agent tested. Water absorption and oil absorption must be low in order to provide commercially acceptable leathers and it is clear that the compounds of this invention offer a significant improvement over the sulfonamide types.

Effect on paper.—Table II which follows indicates the oil resistance of unbleached kraft paper treated with the compounds of the invention in accordance with the above described tests using 0.25% of the treating bath of a nonionic surfactant (t-dodecylmercaptan condensed with 9 moles of ethylene oxide):

TABLE II

Compounds tested: Chrome complex of a mixture of 3 parts $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_7\text{CONHCH}_2\text{COOH}$ and 2 parts $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_9\text{CONHCH}_2\text{COOH}$
 5 Molar ratio of chromium to acid : 3 : 1
 Applied from isopropanol solution to one side of paper and treated side exposed to oil

Percent solids on paper	Time to 50% penetration	
	Peanut oil	Paraffin oil
1.00.....	>1,000 hrs.....	>1,000 hrs.
0.75.....	>1,000 hrs.....	>1,000 hrs.
0.50.....	>1,000 hrs.....	>1,000 hrs.
0.25.....	>48 hrs.....	>30 min.

In another test procedure without surfactant and using turpentine, which is most difficult to keep from penetrating paper, the following results were obtained:

TABLE III.—EVALUATION OF CHROME COMPLEXES ON UNSIZED BLEACHED KRAFT PAPER

Compound Tested	Chrome to acid ratio	Percent solids on paper						
		0.05	0.1	0.2	0.25	.50	.75	1.0
		Time for Penetration of Turpentine to 50% of Surface Area						
Isopropanol solution of chrome complex of $\text{C}_8\text{F}_{17}\text{CONH}-\text{CH}_2-\text{COOH}$.	3:1	3 sec....	18 min....	46 hrs....	73 hrs....	21 hrs....	0.
Isopropanol solution of chrome complex of $\text{C}_{10}\text{F}_{21}\text{CONH}-\text{CH}_2-\text{COOH}$.	3:1	3 sec....	3 hrs....	103 hrs....	117 hrs....	94 hrs....	15 min.
Fluorocarbon acid-amide mixture (see Note 1).	3:1	0.....	0.....	110 hrs....	140 hrs....	140 hrs....	120 hrs....	1 min.
Fluorocarbon sulfonamide (see Note 2).....	3:1	0.....	10 sec....	26 hrs....	14 hrs....	16 hrs....	6 hrs....	0.

NOTE 1.—Isopropanol solution containing a chromium complex of a mixture of $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_7\text{CONHCH}_2\text{COOH}$ and $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_9\text{CONHCH}_2\text{COOH}$ in a weight ratio of 3:2.

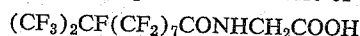
NOTE 2.—Isopropanol solution containing a chromium complex of $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}-\text{CH}_2\text{COOH}$.



The above table clearly indicates the superior repellency properties imparted to paper by the compounds of the invention. Comparing the fluorocarbon acid-amides of the invention at 3:1 chromium ratios with the sulfonamide type, it is readily seen that the repellency obtained with the compounds of the invention is vastly superior. It is also of interest to note that best effects are obtained at from about 0.2 to 0.5% by weight of solids on the treated paper.

50 In a similar test with the fluorocarbon acid-amide used at a chrome to acid ratio of 2:1, excellent results were likewise obtained.

Another test was carried out on sized unbleached kraft paper with chrome complexes of a mixture of



and $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_9\text{CONHCH}_2\text{COOH}$ where the weight ratio of amido-acid components was 2:1 and the chrome to acid molar ratio was 6:1. The test mixture was applied from an isopropanol solution containing 0.25% by weight of the treating bath of a nonionic surfactant (condensation product of t-dodecyl mercaptan with 9 moles of ethylene oxide). Table IV which follows indicates the results obtained:

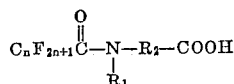
TABLE IV

Percent solids on paper.....	Time for Penetration to 50% of Surface of Treated Paper (Hours)	
	0.29	0.58
Penetration of— Peanut Oil.....	>1,000	>1,000
Paraffin Oil.....	>1,000	>1,000

It will be understood that numerous changes and variations may be made from the above description and examples without departing from the spirit and scope of the invention.

We claim:

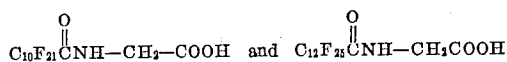
1. Chromium coordination complexes of compounds of the formula



where $\text{C}_n\text{F}_{2n+1}$ is perfluoroalkyl, n is an integer from 8 to 12, R_1 is selected from the group consisting of hydrogen and alkyl having from 1 to 4 carbon atoms, and R_2 is alkylene having from 1 to 6 carbon atoms.

2. Chromium coordination complexes as in claim 1 where R_1 is hydrogen and R_2 is methylene.

3. A mixture of chromium coordination complexes comprising chromium complexes of fluorocarbon acid amides of the formula



wherein the molar ratio of chromium to fluorocarbon acid amides ranges from about 3:1 to about 30:1.

4. A mixture of chromium coordination complexes as in claim 3 wherein the weight ratio of

$\text{C}_{10}\text{F}_{21}\overset{\text{O}}{\parallel}\text{CNH}-\text{CH}_2-\text{COOH}$ to $\text{C}_{12}\text{F}_{25}\overset{\text{O}}{\parallel}\text{CNH}-\text{CH}_2\text{COOH}$ is between about 3:2 to 2:1 and the molar ratio of chromium to fluorocarbon acid amides ranges from about 3:1 to about 6:1.

5. A chromium coordination complex of $\text{C}_8\text{F}_{17}\text{CONHCH}_2\text{COOH}$

10 wherein the molar ratio of chromium to fluorocarbon acid amine is from about 2:1 to about 6:1.

6. A chromium coordination complex of $\text{C}_{10}\text{F}_{21}\text{CONHCH}_2\text{COOH}$

15 wherein the molar ratio of chromium to fluorocarbon acid amide is from about 2:1 to about 6:1.

7. A chromium coordination complex of $\text{C}_{12}\text{F}_{25}\text{CONHCH}_2\text{COOH}$

20 wherein the molar ratio of chromium to fluorocarbon acid amide is from about 2:1 to about 6:1.

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F. A. MIKA, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

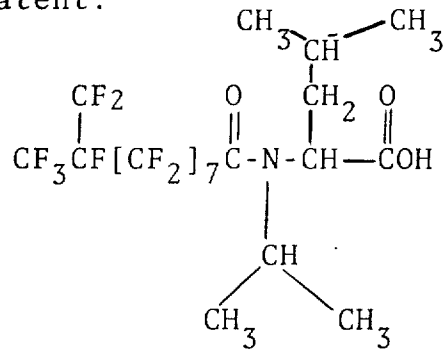
Patent No. 3,351,643

November 7, 1967

Murray Hauptschein et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, lines 1 to 8, the formula should appear as show below instead of as in the patent:



same column 3, line 43, for "genenerally" read -- generally --
column 4, line 42, for "amide-acid" read -- amido-acid --;
column 6, line 37, for "same" read -- sample --; line 43,
for "consist" read -- consists --; column 12, line 11, for
"amine" read -- amide --.

Signed and sealed this 3rd day of December 1968.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents