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ANTIFOULING PAINT

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This invention relates to an antifouling paint and has for its object to obtain a paint which is less injurious to a person and maintains its antifouling property for a long period without decomposition and flowing of the effective ingredients.

An antifouling paint according to this invention comprises as the antifouling ingredients one or more ω -fluoro aliphatic compounds such as $F(CH_2)_{2n-1}COOH$, $F(CH_2)_{2n}OH$ and their derivatives, where n is an integral number larger than 1.

The abovementioned fluoro compounds are called generally as "fluoroacetates" and they are obtained by the reaction of the corresponding halogen compounds with fluoride of silver, mercury, antimony or potassium, respectively, or derived from other fluoro compounds. The aliphatic compounds in which an atom of fluorine is combined at ω -position, show the characteristic antifouling effect, while the compounds in which an atom of fluorine being combined at any position other than ω -position or in which two or more atoms of fluorine are combined, lose almost all antifouling effect. On the other hand, the compounds of which n is the abovementioned formula is 3, show the highest antifouling effect. So in my invention, ω -fluoro aliphatic compounds of which n is one to six, are preferably used. As ω -fluoro aliphatic compounds, I can use acids, alcohols and their derivatives such as salts, nitriles, esters, ethers, acetals, amides, hydrazides, ketones, aldehydes and amines; the important compounds are mentioned as follows:

2-fluoroethanol	$F(CH_2)_2OH$.
4-fluorobutanol	$F(CH_2)_4OH$.
2-fluoroethyl fluoroacetate	$FCH_2COO(CH_2)_2F$.
2-chloroethyl fluoroacetate	$FCH_2COO(CH_2)_2Cl$.
2-fluoroethyl 5-fluorocaproate	$F(CH_2)_5COO(CH_2)_2F$.
Glycol bisfluoroacetate	$(FCH_2COO)_2C_2H_4$.
Glycerol trisfluoroacetate	$(FCH_2COO)_3C_3H_5$.
Fluoroacetic acid	FCH_2COOH .
3-fluoro butyric acid	$F(CH_2)_3COOH$.
Fluoroacetoaldehyde	FCH_2CHO .
Fluoroacetone	FCH_2COCH_3 .
2-2' difluoroethylether	$F(CH_2)_2O(CH_2)_2F$.
Bis fluoroethylacetal	$CH_3 \cdot CH(OCH_2CH_2F)_2$.
Fluoroacetoamide	FCH_2CONH_2 .
Fluoroacetoanilide	FCH_2CONH 
Phenylhydrazine fluoroacetate	$FCH_2CONH-NH$ 
1-amino-2-fluoroethane	$F(CH_2)_2NH_2$.
Fluoroacetonitrile	FCH_2CN .
Sodium fluoroacetate	FCH_2COONa .
Barium fluoroacetate	$(FCH_2COO)_2Ba$.

They are colorless and transparent liquids or crystals and some of them have a faint ester odor. Most of them dissolve easily in alcohols, ethers, aldehydes and esters, especially easily in animal and vegetable oils and fats and varnishes. By reason of their oil solubility or great affinity for oil, the paint obtained is characterized by the absence of separation of the effective ingredients, and ease

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of application. The usual antifouling paints containing heavy metals, such as copper, mercury or compounds of these metals, as the antifouling ingredients have a tendency to separate out, and are difficult to apply, especially by spray-coating.

The said ω -fluoro compounds show high toxic character for all animals, and are particularly fatal to insects and shell-fishes even at extremely low concentration, but they show on a person relatively low toxic character without accumulative property such as the toxic symptom due to heavy metal. Moreover, because of the very stable combination of fluorine atom with carbon atom, the said compound is also very stable and does not lose its toxic character for a long period even in sea water. Accordingly, the paint of my invention shows high antifouling effect for a long period of more than eight months by the stability and absence of flowing of the effective ingredients.

In my invention, an antifouling paint is obtained by kneading said ω -fluoro aliphatic compound, pigment and varnish in a milling machine. As the antifouling ingredient, one or more compounds of the abovementioned ω -fluoro compounds such as acid, alcohol, salt, nitrile, ester, ether, acetal, amide, hydrazide, ketone, aldehyde and amine are used, and oil varnish, natural and artificial resin, shellac and also coal tar, pitch, wood tar are used as varnish in this paint. The usual antifouling ingredient such as cuprous oxide, mercuric oxide and pentachlorophenol may be mixed in my paint, and also my paint may be mixed with the usual antifouling paint.

Example 1

	Parts
2-fluoroethyl fluoroacetate	10
Pigment	45
Oil varnish	45

Example 2

	Parts
2-fluoroethyl 5-fluorocaproate	3
Pigment	45
Polyvinyl varnish	52

Example 3

	Parts
Glycol bisfluoroacetate	15
Pigment	45
Shellac varnish	40

Example 4

	Parts
Monofluoroacetamide	15
Solid cream of zinc oxide	45
Shellac varnish	40

Example 5

	Parts
Phenylhydrazine fluoroacetate	10
Solid cream of zinc oxide	45
Artificial resin (polymerized benzyl chloride)	15
Benzol	30

Example 6

	Parts
Copper monofluoroacetate	20
Pigment	30
Oil varnish	50

In each of the abovementioned examples, all materials were mixed and kneaded in a milling machine and the antifouling paint was obtained.

An iron plate was coated with the paint obtained and steeped in sea water. The plate was completely protected from the adhesion of shell-fish and other marine organisms for eight months.

What I claim is:

1. An anti-fouling paint consisting essentially of varnish, pigment and an ω -fluoroalkyl compound selected from the group consisting of ω -fluoroalkanoic acids, ω -fluoroalkyl alcohols, salts of ω -fluoroalkanoic acids, ω -fluoroalkyl nitriles, ω -fluoroalkyl esters, ω -fluoroalkyl ethers, ω -fluoroalkyl acetals, ω -fluoroalkanoic acid amides, ω -fluoroalkyl hydrazides, ω -fluoroalkyl ketones, ω -fluoroalkyl aldehydes and ω -fluoroalkyl amines. 5
2. An anti-fouling paint according to claim 1, the alkyl of the fluoroalkyl containing one to twelve carbon atoms. 10
3. An anti-fouling paint according to claim 2, the alkyl of the fluoroalkyl containing six carbon atoms.
4. An antifouling paint according to claim 2, the

alkanoic group of the fluoroalkanoic radical containing six carbon atoms.

References Cited in the file of this patent**UNITED STATES PATENTS**

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