

## FLUORINE CONTAINING POLYMER MATERIALS BASED ON UNSATURATED ACIDS MODIFIED ACCORDING TO ESTER FRAGMENT AND THEIR PRACTICAL APPLICATION

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*Here we discuss the approach to the fluorine modification of acrylates and maleates ester fragment using partly fluorinated alcohols and acrylic, methacrylic and maleic acids' derivative synthesize them. We also discuss the reactions involving multiply bond and carboxylic group maleic acid fluorine containing mono-ester and acrylic acid esters. We analyze acrylic polymerization processes their co-polymerization with other olefines, and also fluorine containing polymers' characteristics. We also take a look at practical application fields of such polymer materials.*

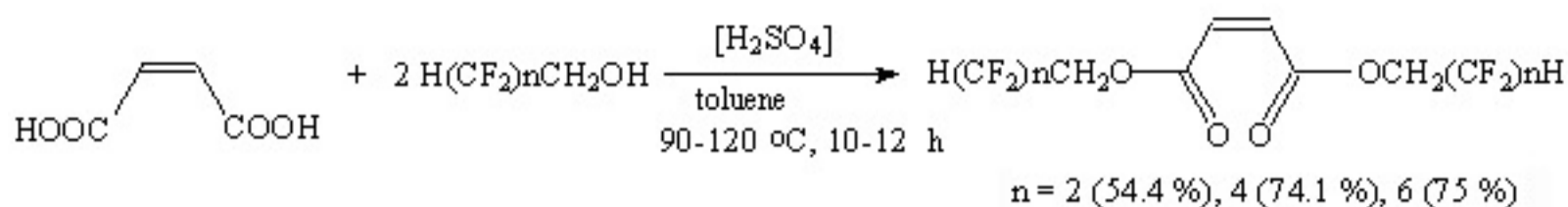
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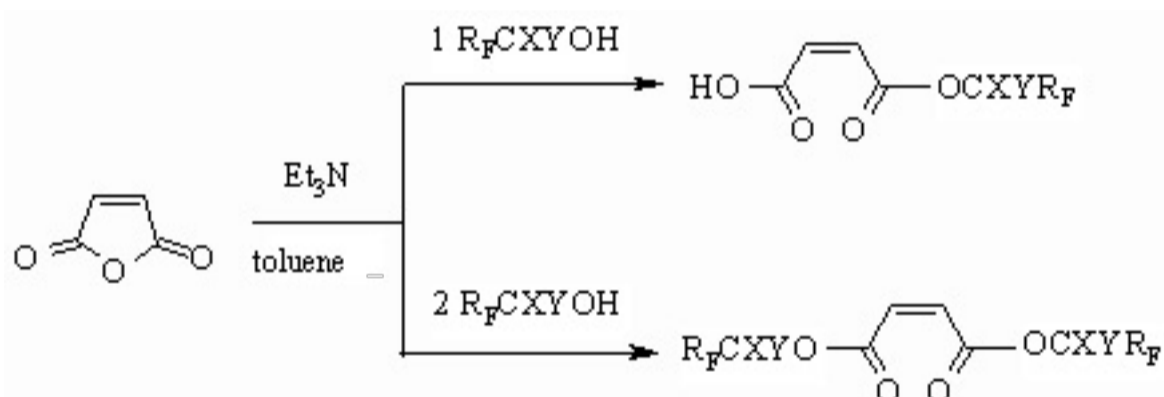
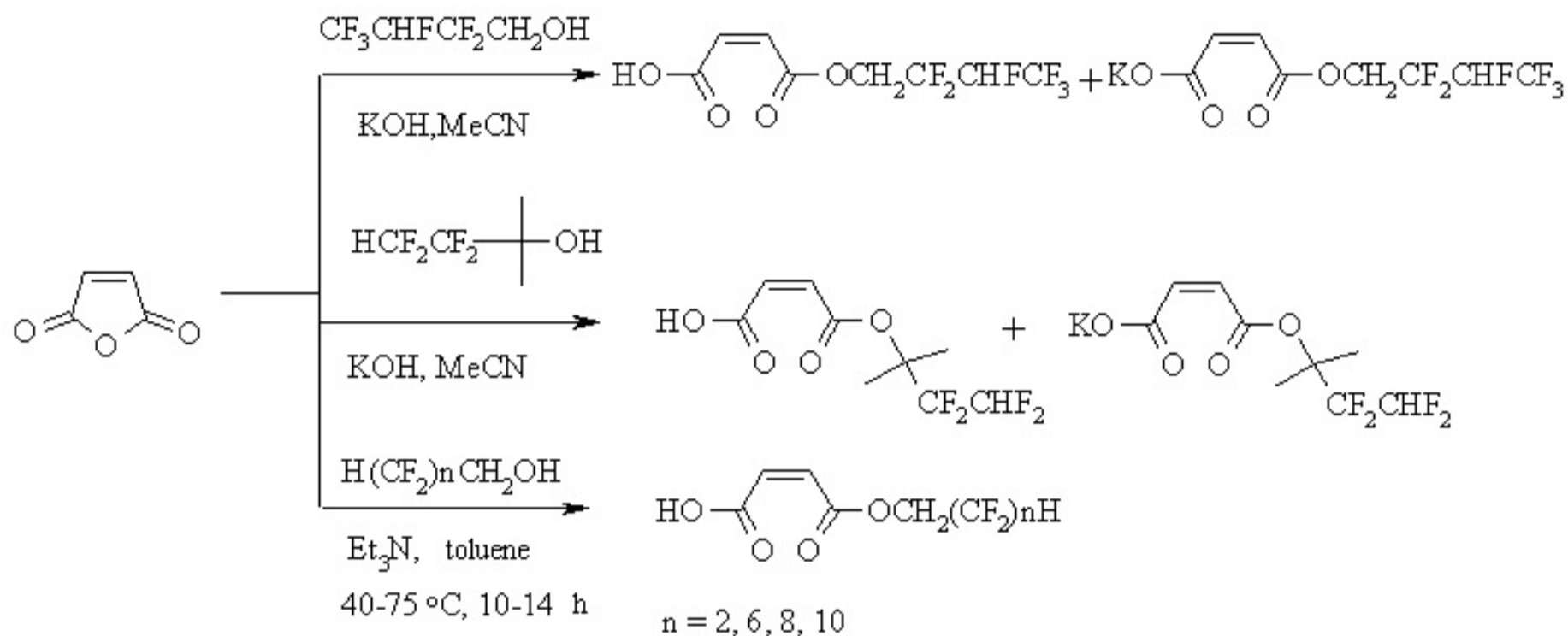
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### **2. Maleic Acid Fluorine Containing Mono- and Diesters Obtaining**

Another unsaturated acid - maleic acid as acrylic acid at catalysts' presence (concentrated sulfuric acid and sulfonated coal) reacts with fluoroorganic alcohol benzene or toluene medium, producing fluoroorganic esters [83,107,108].

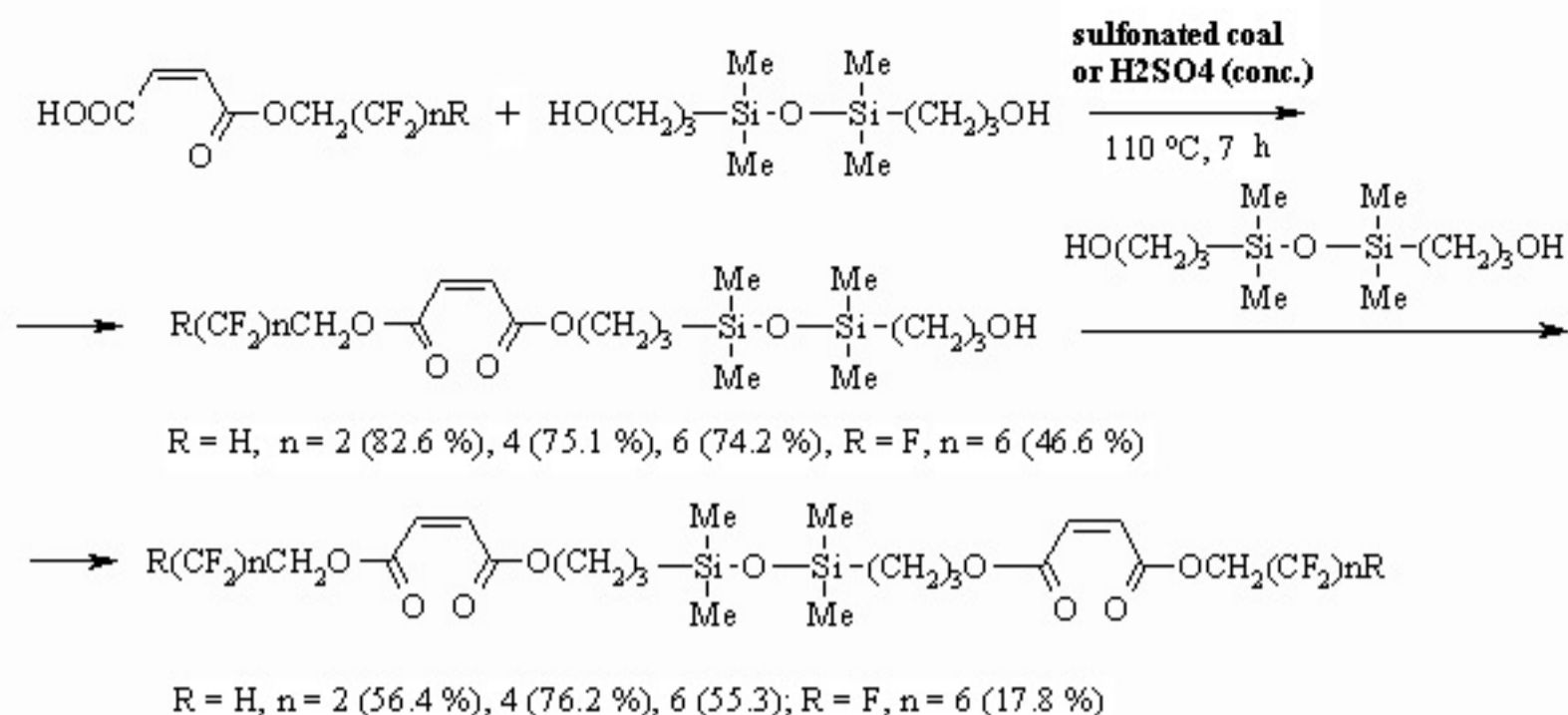


When using maleic acid anhydride fluorine containing mono- and diesters of maleic acid are formed depending on reagents' ratio [109-112]



$\text{R}_f$  X, Y =  $\text{CF}_3\text{CHFCH}_2$ , X=Y=H **a**,  $\text{HCF}_2\text{CF}_2\text{CF}_2$ , X=Y=H **b**,  
 $\text{CF}_3(\text{CF}_2)_5$ , X=Y=H **c**,  $\text{H}(\text{CF}_2\text{CF}_2)_4$ , X=Y=H **d**,  
 $\text{CF}_3\text{CHFCH}_2$ , X=H, Y = Me **e**,  $\text{CF}_3\text{CHFCH}_2$ , X=Y = Me **f**,  
 $\text{HCF}_2\text{CF}_2$ , X=Y = Me

Esterification of fluoroalkoxymaleates acidic esters using 1,3-bis(hydroxypropyl)-1,1,3,3-tetramethyldisiloxane in ratio 1:1 and 2:1 allows to obtain fluorocontaining, organosilicon maleates [113].



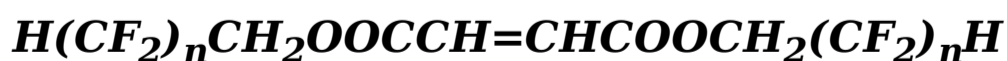
Maleic acid mono-esters salts are surfactants. They are obtained glycltrimethylammonium chloride reaction with mono-ester in dimethylforman [110].

### 3. Sulphuric Acid Derivatives Synthesis Based on Fluorine Contain Ethers of Acrylic, Methacrylic and Maleic Acids and Their Salts.

An interest to surfactants based on fluororganic compounds aroused because their wide application in may fields of economy. Adsorbing at border of phase bre they sharply change the nature and characteristics of surfaces. Creating of coating and films at different organic and non-organic materials is in many aspects determined by adhesive and rheological characteristics of system, contain fluororganic components. Perfluorosulfoacids, perfluorosulfates, dodecylsuccin bis-perfluorocetyl ether and others are used as surfactants. The surface tension studies of a number of acrylic and methacrylic acid fluororganic esters revealed their high surface-active characteristics.



R	n	Yield, %	$\sigma_{20}$ (mH/m)	$-b \cdot 10^2$ [mH/(m.degree)]
H	2	34.0	25.44	10.74
H	4	38.5	23.87	9.50
H	6	45.2	23.61	8.98
Me	4	56.0	23.71	9.17
Me	6	50.8	23.40	8.31



n	Yield, %	$\sigma_{20}$ (mH/m)	$-b \cdot 10^2$ [mH/(m.degree)]
2	54.4	31.21	10.01
4	74.1	27.57	8.90
6	75.0	25.81	7.89

Surface tension  $\sigma$  dependence on temperature  $t$  is approximized by linear equation

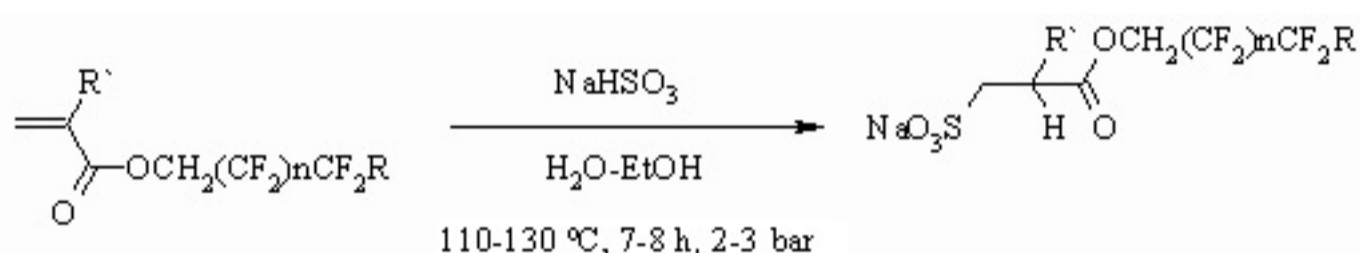
(average ratio error is 0.2 %) :

$$\sigma_t = \sigma_{20} + b(t - 20)$$

By increasing of a number of CF<sub>2</sub> -groups surface tension and its temperature coefficient decrease, at that for methacrylates the tension is somewhat lower, than for acrylates with the same number of CF<sub>2</sub>- groups in chain. Molar surface energy of fluorine derivative acrylates and methacrylates is also arcwise dependant on number of CF<sub>2</sub>- groups.

Sodium and potassium salts of maleic acid mono-esters are used as Surfactants and wetting agents [109].

Sulfopropionic and sulfo-isobutyric acids fluororganic esters salts are of interest of researchers. One of approaches of their synthesis is sodium bisulfite attachment to acrylic and methacrylic acids esters (yield is 64-84 %) [81].



R = H, F; R' = H, Me; n = 3, 5

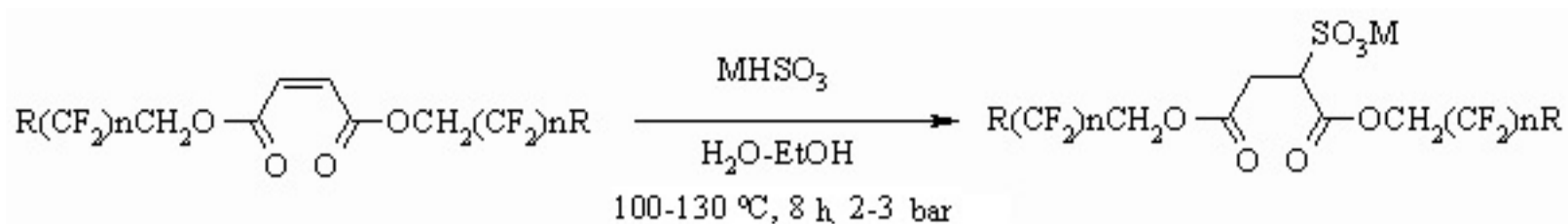
Surface activity of fluoroalkoxysulfopropionates and sulfoisobutyrate with chain length of 5-7 carbon atoms is close to activity of hydrocarboxylic derivative at water-air border.



Salt of common formula			KKM*10 <sup>3</sup> (mol/l)	σ <sub>KKM</sub> (din/cm)	G <sub>KKM</sub> * 10 <sup>-6</sup> (din * cm <sup>2</sup> /mol)
R	R'	n			
H	H	3	17.4	60.0	0.73
H	Me	3	16.9	54.2	1.09
H	H	5	17.3	37.0	2.06
H	Me	5	15.8	31.1	2.63
F	Me	5	7.9	18.0	6.93

The introduction of sodium salt of 1,1-dihydrotridecafluoroheptylsulfobutyrate concentration equal to 8\*10<sup>-3</sup> mol/l leads to decrease of surface tension from 72,7 to 18 and of interfacial tension 34,4 to 15 din/cm, that testifies rather high effectiveness of the present compound as surfactant.

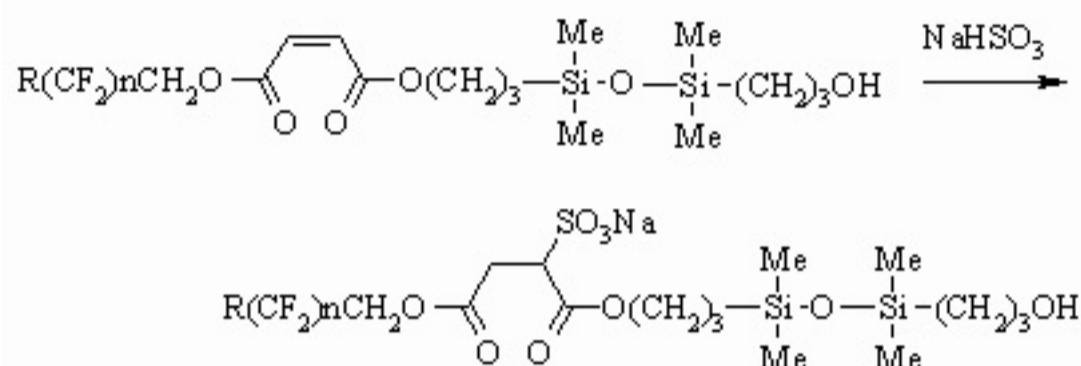
Method was also used for maleic acid di-esters. Thus, the interaction of bis(fluoroalkoxy)maleates and bisulfites of alkali elements results in formation of (fluoroalkoxy)sulfosuccinates salts with the yield of 64-74% [108].



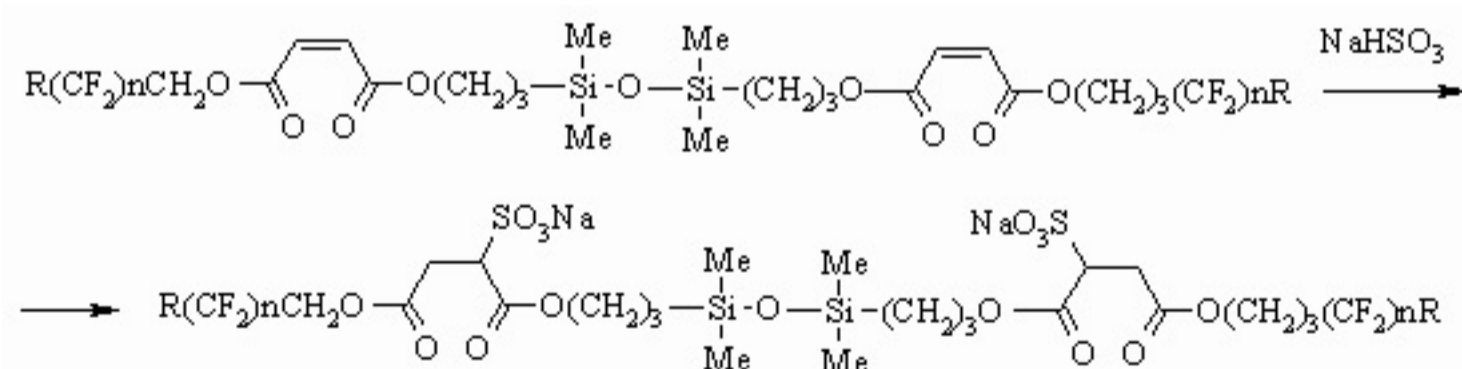
R = H, F; M = Na, K; n = 2, 4, 6

Salts obtained are effective surfactants (for more information please look [114]).

In the work [113] there is a description of sulfosuccinic acid fluorosilicon containing mono- and di-sodium salts, obtained by sodium bisulfite action organofluorosilicon maleates (yield is equal to 55-86 %).



R	n	Yield, %	KKM*10 <sup>3</sup> (mol/l)	σ <sub>KKM</sub> (din/cm)
H	2	86.6	3.71	19.2
H	4	86.4	3.16	18.5
H	6	86.4	2.82	16.0
F	6	70.2	3.16	13.0



R	n	Yield, %	KKM*10 <sup>3</sup> (mol/l)	σ <sub>KKM</sub> (din/cm)
H	2	74.1	2.82	19.8
H	4	65.1	2.69	18.2
H	6	68.0	2.51	16.5
F	6	55.2	3.16	12.5

As we can see from the information above the fluorosilicon containing sulfosuccinic

acid ethers salts are effective surfactants. They while in small amounts (3-4\* mol/l) sharply decrease water surface tension from 72,5 to 12-20 din/cm , interfacial tension (water-oligofluororganosiloxane) from 34,4 to 6-9 din/cm. increasing of fluoroalkyl chain length the surface tension of salts increase.

**To be continued**