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OLEOPHOBIC AND HYDROPHOBIC PROPERTIES OF FLUORO COMPOUNDS AND THEIR APPLICATION IN LEATHER MAKING

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Application of fluoro compounds in leather making is surveyed. The theory behind the oil and water repelling mechanisms of fluoro chemicals is explained. The importance of various types of fluoro chemicals, such as fluro acrylics, copolymers of fluorine containing monomers, fluro silicones, phosphorous containing fluro acrylics is highlighted. Fungicidel and disinfectant properties of fluro compounds on leather are reported. Possible developments and application of these fluro chemicals in leather making are suggested.

Introduction

Interest in fluorine chemistry has increased very much during recent years because of the unusual behaviour often ascribed to materials as a result of introduction of fluorine atom in them. The fluoro chemical industry, however, lagged behind as compared to its halogen members, because of the difficulties in handling hydrogen fluoride.

The main use of fluoro compounds in leather making is to impart oil and water repelling characteristics to leather. Some fluoro compounds have also found application as fungicides in tanneries.

Before directly dealing with their properties and applications it is worth explaining about water and oil repellency and the theory behind these characteristics which make fluoro compounds oil and water repellent.

Fluoro compounds impart hydrophobic (water repelling) and oleophobic (oil repelling) properties simultaneously. This combined effect is called as stain repellency. The stain repellency may be considered as the ability of the material to withstand penetration by liquid stains under static conditions, that is, conditions under which the only forces influencing the penetration of soiling component into the material are capillary forces and the weight of the drop. However, stain resistance of a material is a term used to describe the degree to which a treated material stained under dynamic conditions may be returned to its original unstained appearance by wiping or blotting the surface. Generally stains may be caused by (a) coloured liquids, (b) colourless oils and greases and

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(c) colourless solvents[3]. In the absence of stain repellent treatments oils and oil-based liquid stains spread rapidly over large areas of substrate and invariably render the article soiled.

Physical chemistry of oil and water repellency imparted by fluoro compounds.

Oil repellency is the property which results from the low surface energy of fluorinated films and coatings. Fluorochemical surfaces establish a negative capillary pressure with both aqueous and oily stains[3] and consequently prevent their absorption into treated substrates. Zisman *et al*[4,5] have shown that wettability of low surface energy solids depended directly on the groups of atoms forming the solid surface. Measurement of contact angles (Fig. 1) afforded a means of assessing the wettability of surfaces. In the case of homologous series of organic liquids, it has been shown that a plot of cosine of contact angle θ, against the surface tension of the liquid produces a straight line graph (Fig. 2). The value of surface tension corresponding to line Cos θ = 1 (θ denotes contact angle and hence the condition Cos θ = 1 is equivalent to complete wetting) has been defined as the critical surface tension, γc, of the solid.

Table 1 shows that considerable variations in critical surface tension occur if the groups constituting the surface are changed. In the first example of surface with substituted CF_3 groups, a liquid with a critical surface tension of 6 dynes/cm. or less would be required to wet the surface whereas a liquid with higher surface tension cannot wet it. Substitution of hydrogen for one of the fluorine atoms more than doubles the critical surface tension, and hence such a surface would be more readily wetted. In the last example, (poly (vinylidene chloride) surface) a relatively higher critical surface tension is noted. Thus, other halogen atoms other than fluorine do not provide such low energy surfaces.

TABLE 1

Critical surface tension, γc of low surface energy surfaces

Surface constitution	*γc dynes/cm at 20°C*
$-CF_3$	6
$-CF_2H$	15
$-CF_3$ & $-CF_2-$	17
$-CF_2-$	18
$-CH_2-CF_3$	20
$-CF_2-CFH-$	22
$-CH_3$	22
$-CH_2-$	31
$-CCl_2-CH_2-$	43

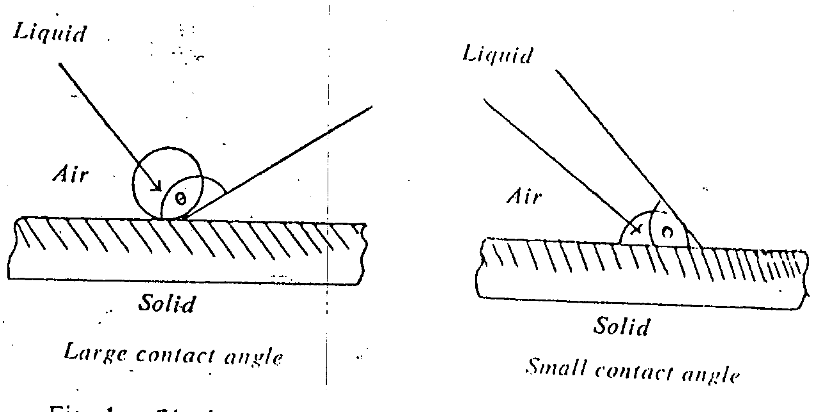


Fig. 1 : The behaviour of drops of the same liquid on films of high and low surface energy solids.

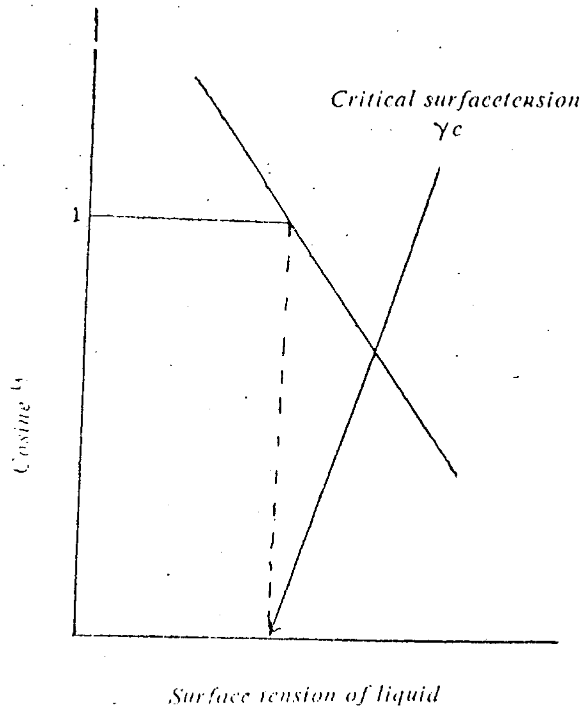


Fig. 2 : A plot of cosine θ *Vs* surface tension of liquid.

Consequently, in order to obtain oil and water repellent property, it is necessary to cover the surface of fibres with closely packed fluorine containing groups such as perfluoro acrylic polymer (Fig. 3)

Development of fluoro chemicals suitable for leather

The products successfully developed and applied were organic acids, containing

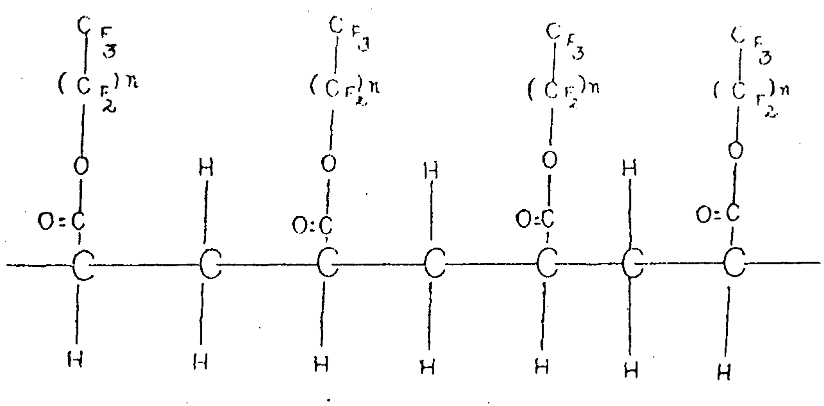
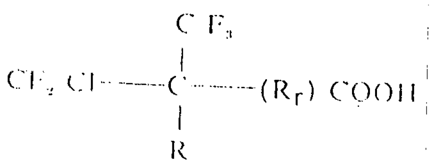


Fig. 3 ; Fluoro polymer

atleast 5 fluorine atoms (for example per fluoro butyric acid). C_3F_7 (OOH) per fluoro acids and their chrome complexes could be applied to suede type of leathers for making them oil and water proof. In making side upper leather[6] with corrected grain oil and water repellent, fluorocompounds are recommended.

Terminally branched and terminally monochlorinated per fluoro carboxylic acids[7] (of the type given below) and their derivatives found use in treating leather surfaces. The treated surfaces were found to have high degree of water repellency at low concentrations and good oil repellency. The leather surfaces are rendered extremely hydrophobic.



Where R_f corresponds to per fluoro alkylene group containing at least 3 carbon atoms.

In lubricating action of alkenyl succinic acid for water repellent leather, Hopkins *et al*[8] have used per fluoro alkyl carboxylic acids and its chromium complexes (Scotch gaurd of Minnesota Mining & Manufacturing Co.) as one of the ingredients in making leather oil and water proof. Scotch gaurd[9] is also recommended during or after finishing operations to get excellent water resistance. A good number of fluoro compounds are reported in literature to be used as water and oil repelling agents in leather industry. A fluorochemical Foraperle C203 that can be applied to both suede and grain leathers to impart water and stain resistance was recently introduced.

Permeable, wettable, permanently water resistant leather can be produced by treating it with the dispersion of 1 (—steramide methyl) pyridinium chloride (1) in water mixed with sodium acetate in water at 110-130°F and combined with an emulsion of perfluoro butyl acrylate (2) at 110-130°F. This dispersion would give better results compared to the treatment of leather with either 1 or 2 alone.[13]

Oil repelling property of polyfluoro compounds is closely related to chain length. Longer chain length lowers the surface energy and confers hydrophobic properties in varying degrees because of CF_3 and a good number of CF_2 sites.

Normally, silicone water repellents cannot be used in conjuction with fluorochemicals as they greatly reduce the oil repellent property of fluoro carbons. This is because of the masking[14] of fluoro alkyl groups and terminal trifluoro methyl groups of the fluoro polymer by a film of silicone polymer, containing liophilic (oil attracting) methyl groups. To overcome this difficulty attempts have been made to make stain-repellent finishes more hydrophobic and more durable by incorporation of fluoro alkyl groups on the silicone atom, through covalent linkages[15,16] and by the preparation of fluoro alkyl siloxane polymer. In the case of grain-finished leathers, soil repellency, wet-rub fastness and heat resistance are important properties. Development of polymers containing per fluoro group suitably oriented for shielding the surface to oil and water molecules and capable of withstanding dry cleaning operation is imperative in the near future.

In the case of fluoro acrylics, fluoro sites are so placed that they form side chains so that the film containing this will be shielded from oil and waters (Fig 4.)

Further, fluorine containing phosphorus compounds also impart oil repellency.

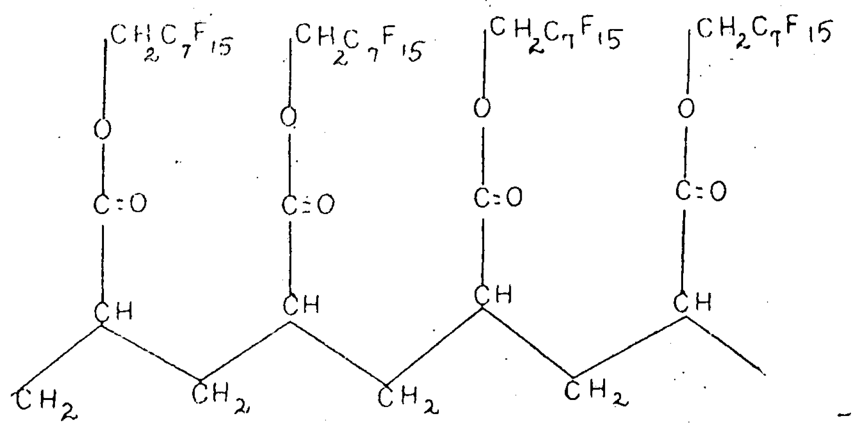


Fig. 4 : Poly acrylate

Poly fluoroalkyl phosphates having medium alkyl chain-length can be applied to leather to impart oil repellency[18]. Products of this type may find place in the manufacture of industrial gloves and garments.

Fluorine containing copolymers

Fluoro polymers of the type per fluoro octyl acrylate methacrylyl chloride copolymer may also be used for making fur stain repellent and shrink resistant.[19] The product is obtained by copolymerising 1, 1 – dihydro per fluoro octyl acrylate and methacrylyl chloride. This reactive polymer (Fig. 5) when applied to fur will react with amino acid hydroxyl groups resulting in desired properties.[20]

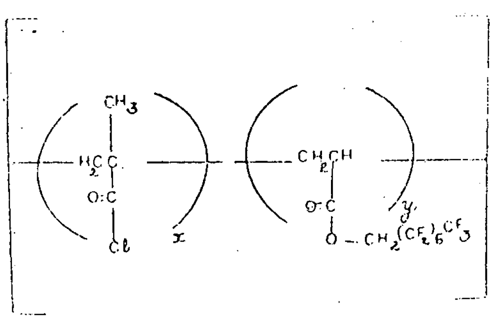


Fig. 5 : Copolymer

Fluoro compounds as fungicides and disinfectants

Fluoro compounds are used as disinfectants to leather[21]. For preventing 'red heat' of brined hides during storage, addition of silicofluoride and sodium pentachlorophenate are recommended. Hides which do not contain either of these disinfectants were poor after storage. Hides treated with Na_2SiF_6 were better. Silicofluoride has been found to be effective to prevent bacterial growth[22]. Accelerated soaking[23] and liming of hides was achieved for heavy upper leather by drumming salted hide splits with Na_2SiF_6.

Fluoro compounds have also found their use in textile, paper and plastic industries. Fluorinated wax,[24] perlluoro alkyl vinyl sulphones[25], poly (2,3 bis hepta fluoroisopropoxy propyl acrylate[26]) etc. imparted oil and waterproofing properties to cotton and paper. Smetz[27] reported a number of perfluoro alkyl – terminated compounds which are useful as oil and water repellent coatings. Such coatings can be extended for leather finishes also. Perfluoro alkyl urea derivatives[28] were found to impart crease resistant property. Finally, fluorine renders plastics, thermally stable and resistant to chemicals. Poly (vinylidene fluoride)[27] dispersion coatings have very much established for excellent exterior durability and chemical resistance. If these are applied on leather, no doubt, one can produce leathers which have to be exposed to environment and open climatic conditions continuously.

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