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# Reduction of Polymeric Friction by Minor Concentrations of Partially Fluorinated Compounds

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## ABSTRACT

A new approach to the reduction of boundary friction in solid polymers has been studied. Dry frictional properties of several classes of polymeric solids have been reduced significantly by the addition of small proportions of a suitably designed surface-active compound. Appropriate fluorocarbon derivatives have been prepared and found effective in polymethyl methacrylate, polyvinyl chloride, and in several polyvinylidene chloride copolymers. These addition agents are effective both in polymer films prepared by evaporation from a solvent and in thick disks prepared from the melt. The low-energy surfaces formed by the fluorinated additives may also be self-healing, that is, any surface-active molecule lost from the film may be replaced by the diffusion of additional material to the interface.

The decrease in friction caused by the addition agent is accompanied by an increase in the equilibrium contact angle of each of several liquids on the polymer surface. The small proportion of addition agent used causes only a small decrease in the hardness of the polymers. There are many promising applications of this technique to specific problems in lubrication and adhesion.

## PROBLEM STATUS

This is an interim report; work on this problem is continuing.

## AUTHORIZATION

NRL Problem C02-03  
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## REDUCTION OF POLYMERIC FRICTION BY MINOR CONCENTRATIONS OF PARTIALLY FLUORINATED COMPOUNDS

### INTRODUCTION

Friction between dry, clean solids is strongly dependent upon both the surface and bulk properties. In general, lowering the free surface energy of a solid ( $\gamma_0$ ), or the critical surface tension of wetting ( $\gamma_c$ ), decreases the specific adhesion and wettability and also lowers the coefficient of sliding friction. This last relationship was established during investigations (2,3) of the friction and wetting of polyethylene and a series of halogenated derivatives of polyethylene. Progressive replacement of hydrogen atoms by fluorine atoms decreased both the coefficient of friction and the critical surface tension of wetting; replacement of hydrogen atoms by chlorine atoms increased these properties.

Despite their high melting points, remarkable chemical stabilities, and low coefficients of friction, fully fluorinated ethylene and propylene polymers, like Teflon and FEP Teflon, have been much limited as lubricating solids by their cold-flow properties and low heat conductivities. Therefore, these polymers have been used primarily as dry film lubricants. Lubricant applications of other polymers of higher strength such as nylon, which is widely used in low-cost bearings and gears, have been limited by their high coefficients of boundary friction.

Many high polymers having greater strength and lower cost than fluorocarbon polymers could become useful as dry lubricating surfaces or as bearing materials if the coefficient of friction could be substantially decreased without proportionately decreasing the bulk strength properties. One approach to the problem would be to search for suitable liquid lubricants. Although the boundary friction between metals can often be greatly reduced by this method, no such approach has been sufficiently effective with polymeric solids. The cause is surface-chemical; it has not been possible to adsorb a close-packed lubricant film on any of the strong, water-insoluble, solid high polymers because the adsorption sites are either not available or are too far apart (4). Another difficulty is that if such sites were formed by surface treatment, they would soon be worn off nearly all organic polymers.

A novel and more promising solution to this problem was made evident by our recent investigation (8) which showed that it was possible to modify the surface properties of many types of polymeric solids by adsorption resulting from addition to the molding material of a small proportion of a partially fluorinated compound having surface activity in an organic medium. Such fluorinated compounds and their surface-active properties in various organic liquids have been described in a series of papers from our Laboratory (1,9-11).

Suitable polymer compositions of this type can be formed either by dissolving the polymer and the fluorocarbon derivative in a volatile solvent or by molding the polymer well mixed with the fluorocarbon derivative. In any case, during molding or during solvent evaporation, some of the molecules of the surface-active compound diffuse to and adsorb at the free surface of the solid. In a recent publication (8), measurements of the contact angles of a series of liquids on these coatings have demonstrated that, with the appropriate concentration of additive in each polymer, the perfluoroalkane groups adsorbed as a close-packed monolayer at the polymer surface. Some of these additives in a concentration of only 1% or less greatly reduced the critical surface tension of wetting of the solid polymer.

For example, 0.5 wt-% of tris(1H,1H-pentadecafluoro-octyl)tricarallylate in polymethyl methacrylate reduced the critical surface tension ( $\gamma_c$ ) from 39 dynes/cm to 19 dynes/cm. Such small concentrations do not alter significantly the bulk physical properties of the polymeric solid.

During the past year we have investigated the influence of these and several newly synthesized addition agents on the frictional and durability properties of various solid polymers. This report will summarize the results to date. Measurements will be given of the changes in wettability not only because of their intrinsic interest but also because they give valuable evidence of the presence, packing, and orientation of adsorbed films of the fluorocarbon additive. Hardness measurements on the plastics with and without additives will be given as convenient evidence of any effect of additives on the bulk strength properties of the plastics.

## EXPERIMENTAL METHODS AND MATERIALS

Friction measurements were made with steel sliding on the solid polymers, pure or modified with an additive, using either of two modified "stick-slip" machines which are essentially the same as that designed by Goodzeit, Hunnicutt, and Roach (6). One specimen was a 1/2-inch-diameter sphere of 52100 steel which was locked in a chuck fastened to the friction arm; the other was either a flat disk of the polymer or a polymer coating on a glass flat which was clamped to a sliding steel table. The normal force, or load, was applied to the ball by means of a cam which depressed the friction arm and pressed together the steel ball and plastic specimen. Relative motion between the steel ball and plastic disk was produced by either an Air-Draulic cylinder or a hydraulic pump which moved the sliding table along a pair of parallel tracks. Two pairs of electrical wire strain gauges, cemented on the friction arm, were used as the force-measuring elements for the load and friction, both of which were recorded simultaneously on a Brush oscillograph. Unless otherwise specified, the static ( $\mu_s$ ) and kinetic ( $\mu_k$ ) coefficients of friction were determined at 25°C; the relative speed of sliding of the specimens was 0.01 cm/sec; and the normal load applied was 1 kg. Hardness was measured with a Vickers 136° diamond pyramid indenter (15). At least three hardness measurements were made at a 100-gram load and three at a 500-gram load, and each load was applied for 15 seconds.

The seven partially fluorinated surface-active compounds used in this investigation are given in Table 1 along with a letter designation for convenience of discussion. Additives A through D are fluorinated esters of high purity which were synthesized at this Laboratory by O'Rear and coworkers (5,12,13) for this and earlier investigations of surface activity in organic liquids and polymers. Several pertinent physical properties of these esters are also listed in Table 1. Additive E, a monochloro derivative of a perfluoroalkane, was a pure research preparation donated by the Pennsylvania Salt Manufacturing Company; the preparation and physical properties have been reported by Hauptschein, et al. (7). Additive F was a telomer of tetrafluoroethylene prepared by the Organic Chemical Department, E.I. du Pont de Nemours and Company, as experimental sample DV9124. Additive G was an experimental fluorochemical made available by the Minnesota Mining and Manufacturing Company. The di(2-ethylhexyl)phthalate used was a commercial grade obtained from the Carbide and Carbon Chemicals Corporation, and it was freed from polar contaminants by slow percolation through a long adsorption column containing activated alumina and Florisil.

The method used to measure the slowly advancing contact angles on the polymer surfaces, as well as the sources, methods of purification, and surface tensions of the liquids used in making the measurements, has been described in numerous reports from this Laboratory over the past 15 years; the significance of the results has been reviewed recently (14,16).

Table 1  
Partially Fluorinated Compounds Used as Surface-Active Additives in Plastics

Brief Designation	Name of Compound	Molecular Wt	Melting Point (°C)	Boiling Point (°C/at mm Hg)	Index of Refraction $n_D^{20}$
A	Bis(1H,1H-pentadecafluoro-octyl) tetrachlorophthalate	1068	65-66	188/0.2	-
B	Bis(1H,1H-pentadecafluoro-octyl) n-octylsuccinate	994	19-22	152/0.1	1.3530
C	Tris(1H,1H-pentadecafluoro-octyl) tricarallylate	1322	ca.45	181/0.2	1.3550*
D	Bis(1H,1H-pentadecafluoro-octyl) 4-chlorophthalate	965	42-48	157/0.1	1.3711*
E	$C_3F_7[CF_2-CF(CF_3)]_4Cl$	805	-	112/10	-
F	Telomer of tetrafluoroethylene	2000-3000	-	-	-
G	$C_8F_{17}SO_2N(C_2H_5)OCN$ (Cyclohexane ring with CH <sub>3</sub> ) $NCO(C_2H_4)N(C_2H_5)SO_2C_8F_{17}$				

\*Index of Refraction for supercooled liquid.

In this investigation five polymers were studied: polymethyl methacrylate, polyvinyl chloride, polyvinylidene chloride, and two copolymers of polyvinylidene chloride, one containing 20 wt-% polyacrylonitrile and the other 15 wt-% polyvinyl chloride. The polymethyl methacrylate used was obtained from E.I. duPont de Nemours and Company as Lucite 41; it was purified by two reprecipitations from tetrahydrofuran solution with methanol and then dried under vacuum for 48 hours. The polyvinyl chloride used was a commercial sample from the Bakelite Division of the Union Carbide and Carbon Corporation, and it was used as received. The polyvinylidene chloride and the two copolymers of polyvinylidene chloride were special research samples furnished by the Dow Chemical Company; they were also used without further purification.

## EXPERIMENTAL RESULTS

### Polyvinylidene Chloride Copolymer Films

Two films of a copolymer containing 80 wt-% vinylidene chloride and 20 wt-% acrylonitrile were deposited by slow evaporation from tetrahydrofuran solutions onto flat-bottom, Pyrex dishes (Knoop hardness 480). One solution contained 1% of additive A; and the other, the control sample, contained no additive. Each film was approximately 15 microns thick. The much greater contact angles of water, methylene iodide, and hexadecane on the film containing additive A (Table 2) indicated the presence of fluorocarbon groups in the surface in agreement with results reported by Jarvis, Fox, and Zisman (8). The decrease in friction caused by the presence of 1 wt-% of additive A was even more remarkable. The static coefficient of friction ( $\mu_s$ ) of 0.80 of the pure polymer is to be compared with the value of 0.10 for the polymer plus additive. The kinetic coefficient of friction ( $\mu_k$ ) decreased correspondingly from 0.65 to 0.08. Thus a 1 wt-% concentration of additive A lowered  $\mu_s$  and  $\mu_k$  by nearly an order of magnitude sufficient to make a good boundary lubricant of the dry solid plastic. Even after 200 reciprocating traverses at 0.10 cm/sec under a load of 1000 grams,  $\mu_k$  had risen to only 0.10. Under a 5000-gram load  $\mu_k$  began to increase rapidly after the first 25 traverses.

Table 2  
Effect of Additive Agent "A" on Wettability and Friction of  
Vinylidene Chloride-Acrylonitrile Copolymer\*

Additive	Contact Angles			Coefficient of Friction†	
	Water	Methylene Iodide	Hexadecane	$\mu_s$	$\mu_k$
None	81°	32°	0°	0.80	0.65
1 wt-% A	101°	51°	43°	0.10	0.08

\*Copolymer studied in form of a film (15 microns thick) on Pyrex glass at 25°C.

†Load of 1 kg on 1/2-in.-diameter 52100 steel ball sliding at 0.10 cm/sec.

### Polyvinylidene Chloride

Polyvinylidene chloride specimens containing additive A were prepared by thoroughly mixing the dry powders of polymer and additive, placing the mixture in a steel mold, and forming a solid disk at 225°F under a pressure of 10,000 psi for six hours. The three contact angles and the coefficients of friction,  $\mu_s$  and  $\mu_k$ , exhibited by disks containing 0, 1, and 2 wt-% of additive A are summarized in Table 3. Contact angles were measured on the smooth, glossy, freshly molded surface of each disk. It is evident from a comparison of the contact angles of water, methylene iodide, and hexadecane on the two types of specimens that the addition of 1 or 2 wt-% of additive A greatly lowered the surface energy of this polymeric solid.

Table 3  
Wettability and Friction of Polyvinylidene Chloride\*

Additive	Contact Angles			Coefficient of Friction†					
	Water	Methylene Iodide	Hexadecane	As Molded		Abraded		Reheated to 50°C	
				$\mu_s$	$\mu_k$	$\mu_s$	$\mu_k$	$\mu_s$	$\mu_k$
None	83°	30°	0°	0.50	0.45	0.40	0.35	-	-
1 wt-% A	104°	49°	29°	0.20	0.15	0.39	0.37	0.23	0.13
2 wt-% A	99°	48°	28°	0.22	0.15	0.39	0.34	0.22	0.14

\*Bulk polymer, all data at 25°C.

†Load of 1 kg on 1/2-in.-diameter 52100 steel ball sliding at 0.01 cm/sec.

Three surface conditions of each disk were studied in measuring the coefficients of friction. In Table 3 the column headed "As Molded" refers to a freshly molded disk with a smooth, glossy surface. The column headed "Abraded" refers to the disk surface after having been gently abraded under water on 600A-grit silicon carbide paper and then dried in a clean desiccator for at least one hour. In order to avoid contaminating the specimen during abrasion, each disk was handled with clean polyethylene gloves or with clean platinum-tipped tongs. The column headed "Reheated" refers to disks which, after abrasion, had been placed in an oven at 50°C for several hours in closed, acid-cleaned, dry, glass containers. No friction measurements were made until the disks had cooled to 25°C.

Table 4  
Frictional Durability of Polyvinylidene Chloride  
Modified by Additive A\*

Traverse No.	Coefficient of Friction†	
	$\mu_s$	$\mu_k$
1	0.25	0.14
3	0.14	0.12
10	0.12	0.12
50	0.12	0.12
200	0.13	0.13
350	0.16	0.14
500	0.17	0.14
600	0.17	0.15

\*Bulk polymer specimen containing 1 wt-% Additive A after abrasion and storage at 50°C for 4 hr.

†Load of 1 kg on 1/2-in. steel ball 52100 steel sliding at 0.10 cm/sec and 25°C.

Friction of the freshly molded disk of pure polyvinylidene chloride was very high ( $\mu_s = 0.50$  and  $\mu_k = 0.45$ ), and "stick-slip" motion was observed in the friction machine. Incorporation of 1 or 2 wt-% of additive A reduced friction by 56% to 66%. After the surface of the nonadditive disk was abraded, friction decreased; this decrease was probably the result of the removal of the softer, more amorphous, surface layer frequently produced in molding plastics (3). Abrasion greatly increased the friction of the two disks containing additive A. Evidently, much of the adsorbed film of additive A was removed with the outer layer of plastic, for after abrasion the coefficients of friction of all three samples were nearly equal. However, the additive present in the bulk phase can diffuse to the surface, adsorb, and reform the equilibrium fluorocarbon film, and therefore can again cause a reduction in friction. This self-repair process could be produced by heating the disk at 50°C for several hours; thus, values of  $\mu_s$  and  $\mu_k$  measured after heating the disks containing additive A were nearly equal to those of the "As Molded" surfaces.

Contact angles and coefficients of friction of the disks containing 1 and 2 wt-% of additive A were practically identical (Table 3), indicating that the adsorption of fluorocarbon derivative A at the polymer surface had reached a maximum for a concentration of 1 wt-%. Sufficient additive remained in the bulk polymer so that the adsorbed film could be removed and replaced many times by successively abrading and reheating the plastic specimens. However, the film was very slowly repaired by adsorption when the disk was stored at temperatures below 50°C. For example, an abraded disk containing 1 wt-% of additive A exhibited an initial  $\mu_k$  value of 0.37 which decreased through adsorption to 0.27 after 16 hours at 41°C, but which remained 0.37 after many days at 25°C.

Table 4 shows that the adsorbed film of additive A can be very durable. After the abraded surface had become coated with the film by regeneration during storage of the disk at 50°C for four hours, both  $\mu_s$  and  $\mu_k$  decreased after the first traverse, remained at a constant minimum of 0.12 to 0.14 for the next 200 traverses, and then slowly increased; even after 600 traverses,  $\mu_k$  was only 0.15 and  $\mu_s$ , 0.17. The pressure of the steel slider on the disk, as estimated from the track width, was 9000 psi. Such durability indicates useful possibilities of the principles being demonstrated. The large decrease in  $\mu_s$  after the first traverse indicates some transfer of the fluorocarbon additive to the steel slider during initial sliding.

## Vinylidene Chloride-Vinyl Chloride Copolymer

Disks of copolymers of 85 wt-% vinylidene chloride and 15 wt-% vinyl chloride were molded from well-mixed powdered polymer and additive at 160° F and 10,000 psi for 4-1/2 hours. Fluorinated compounds A, D, E, F, and G, as well as one widely used plasticizer, di(2-ethylhexyl)phthalate (DOP), were investigated as addition agents. Vickers hardness numbers, contact angles for three liquids, and coefficients of friction for each disk are given in Table 5. The three surface conditions for friction indicated in the column headings are those described in the preceding section. In Table 5, as well as in Tables 6 and 7, friction coefficients in the column headed "Reheated" were all measured after the disks were stored at 50°C for 18 hours.

Coefficients of friction of the original, molded, nonadditive disk were high, and they remained essentially unchanged after abrading and reheating the disk. Presence in the plastic of 1 wt-% of additive A caused an 11% decrease in the hardness number, an increase of at least 40% in the contact angles for the three liquids, and decreases of 75% and 83% in the values of  $\mu_s$  and  $\mu_k$  of the "As Molded" disk. When the newly molded disk was abraded, the adsorbed film of additive A must have been almost completely removed from the surface, since the values of  $\mu_s$  and  $\mu_k$  became nearly identical with those obtained with an abraded surface of the pure polymer. After this abraded surface was reheated,  $\mu_k$  decreased to 0.17 and  $\mu_s$  reached only 0.28; hence, the coefficients of friction had not returned to the low values of the original surface. After this same disk had been stored in a closed glass container for an additional 23 days at 25°C, no further decreases in the coefficients of friction resulted. Storage of the disk at 80°C for 65 hours did not cause further changes in  $\mu_s$  and  $\mu_k$ , i.e., they remained at 0.28 and 0.17. This experiment again illustrates that after the surface film has been removed by abrasion it can be partly regenerated by exposure at slightly elevated temperatures.

Addition of 1 wt-% of plasticizer DOP decreased the hardness number by 17%; the same weight concentration of additive A decreased it by 11%. The contact angle of water was raised 12% by 1 wt-% DOP; it was raised 40% by 1 wt-% of additive A. The contact

Table 5  
Hardness, Wettability, and Friction on Vinylidene Chloride-Vinyl Chloride Copolymer\*

Additive	Vickers Hardness Number	Contact Angles			Coefficient of Friction†					
		Water	Methylene Iodide	Hexadecane	As Molded		Abraded		Reheated to 50°	
					$\mu_s$	$\mu_k$	$\mu_s$	$\mu_k$	$\mu_s$	$\mu_k$
None	16.7	80°	31°	0°	0.49	0.46	0.49	0.45	0.46	0.45
1 wt-% A	14.8	111°	60°	30°	0.12	0.08	0.46	0.41	0.28	0.17
1 wt-% DOP	13.9	90°	28°	0°	0.30	0.22	0.45	0.43	0.43	0.47
5 wt-% DOP	9.7	90°	21°	0°	0.27	0.20	0.41	0.37	0.49	0.47
20 wt-% DOP	5.3	-	-	-	0.33	0.25	0.45	0.42	0.54	0.50
1 wt-% A plus 1 wt-% DOP	14.4	106°	52°	38°	0.20	0.09	0.41	0.34	0.41	0.35
1 wt-% A plus 5 wt-% DOP	4.9	113°	52°	36°	0.21	0.13	0.41	0.34	0.47	0.34
1.4 wt-% D	17.3	97°	49°	30°	0.26	0.11	0.33	0.20	0.30	0.18
0.9 wt-% E	15.6	92°	30°	0°	0.45	0.41	0.47	0.44	0.48	0.37
2.2 wt-% E	15.5	92°	30°	0°	0.44	0.44	0.45	0.39	0.44	0.36
2 wt-% F	15.9	93°	63°	30°	0.25	0.04	0.34	0.13	0.34	0.14
2 wt-% G	15.7	-	-	-	0.27	0.27	0.42	0.40	0.42	0.41

\*Bulk copolymer, all data at 25°C.

†Load of 1 kg on 1/2-in. 52100 steel ball sliding at 0.01 cm/sec.

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Table 6  
Hardness, Wettability, and Friction of Polyvinyl Chloride\*

Additive	Vickers Hardness Number	Contact Angles			Coefficient of Friction†					
		Water	Methylene Iodide‡	Hexadecane	As Molded		Abraded		Reheated to 50°	
					$\mu_s$	$\mu_k$	$\mu_s$	$\mu_k$	$\mu_s$	$\mu_k$
None	14.3	75°	20°	0°	0.50	0.42	0.39	0.34	0.46	0.37
1 wt-% A	14.2	96°	29°	15°	0.30	0.13	0.38	0.31	0.33	0.18
2 wt-% A	14.2	98°	29°	19°	0.37	0.16	0.41	0.30	0.32	0.18
1 wt-% DOP	13.3	89°	25°	0°	0.32	0.24	0.36	0.28	0.36	0.33
5 wt-% DOP	9.8	96°	24°	0°	0.22	0.21	0.30	0.22	0.38	0.31
1 wt-% A plus 1 wt-% DOP	12.8	101°	27°	14°	0.28	0.17	0.33	0.21	0.33	0.20
2 wt-% A plus 5 wt-% DOP	10.1	114°	-	12°	0.21	0.18	0.27	0.20	0.31	0.21

\*Bulk polymer, all data at 25°C.

†Load of 1 kg on 1/2-in. 52100 steel ball sliding at 0.01 cm/sec.

‡Methylene iodide appears to attack the PVC surface.

Table 7  
Hardness, Wettability, and Friction of Polymethyl Methacrylate\*

Additive	Vickers Hardness Number	Contact Angles			Coefficient of Friction†					
		Water	Methylene Iodide	Hexadecane	As Molded		Abraded		Reheated to 50°	
					$\mu_s$	$\mu_k$	$\mu_s$	$\mu_k$	$\mu_s$	$\mu_k$
None	25.1	78°	37°	0°	0.60	0.52	0.54	0.48	0.53	0.47
2 wt-% B	23.3	84°	43°	21°	0.34	0.16	0.35	0.32	0.34	0.27
4 wt-% B	20.7	88°	46°	23°	0.33	0.14	0.27	0.15	0.25	0.15
4 wt-% C	22.2	92°	61°	53°	0.19	0.12	0.29	0.19	0.21	0.15
2 wt-% C plus 5 wt-% DOP	19.7	101°	59°	52°	0.19	0.10	0.23	0.17	0.23	0.16

\*Bulk polymer, all data at 25°C.

†Load of 1 kg on 1/2-in. 52100 steel ball sliding at 0.01 cm/sec.

angle of methylene iodide was actually lowered 10% by 1 wt-% DOP, whereas it was raised 100% by 1 wt-% additive A. This is a dramatic demonstration that fluorocarbon "tails" of additive A lie in the surface. Finally, the hexadecane contact angle was not altered by 1 wt-% DOP; but it was raised from 0° to 30° by 1 wt-% of additive A. The addition of 1 wt-% DOP was not nearly as effective in decreasing  $\mu_s$  or  $\mu_k$  as 1 wt-% A. Some DOP was lost from the specimens during the molding process; hence, the 5-wt-% and 20-wt-% disks actually contained appreciably less than these amounts. Abrading the surface of each molded disk which contained DOP caused  $\mu_s$  and  $\mu_k$  to return to the high values characteristic of the nonadditive disk, but reheating the disk did not cause a decrease in the friction coefficients.

Incorporation of both additive A and DOP in the polymer resulted in softening the disk, increasing the contact angles, and causing a lowering in the coefficients of friction; the effect was usually intermediate between that caused by each additive when used alone. After these surfaces were abraded, friction increased, but not to the same extent as it had with the other disks. A small amount of the additives may still have remained in the surface of the disk. Heating the disk did not cause a reduction in friction, indicating that DOP inhibited the migration of the surface-active additive to the surface of the plastic.

Additive D differs from additive A only in that the former has one chlorine atom on the 4 position of the benzene ring structure, whereas the latter has chlorine atoms at three additional positions, the 3rd, 5th, and 6th. Additive D caused lower contact angles and higher coefficients of friction than the same weight concentration of additive A. The relatively lower values of  $\mu_k$  for the abraded disk containing additive D than for that containing additive A indicate that either D was not completely removed from the surface by abrasion or that it rapidly rediffused to the surface at room temperature. Additive E in both 0.9-wt-% and 2.2-wt-% concentrations was much less effective in altering the contact angles than A or D, and it was completely ineffective in altering  $\mu_s$  and  $\mu_k$ ; hence the wettability and friction of these disks were essentially those of the pure polymer.

The kinetic coefficient of friction  $\mu_k$  on the freshly molded surface of the disk containing 2 wt-% additive F was the lowest obtained in this study. After the surface was abraded, friction increased. The value of  $\mu_k$  was 0.25 when sliding commenced, but it decreased rapidly with sliding distance to an equilibrium value of 0.10 after 2 mm. The value of 0.13 given in Table 5 is the average over the first 4 mm of sliding. The decrease in  $\mu_k$  with sliding distance was probably a result of transfer of the additive from the disk to the steel slider, because when the same slider was made to traverse either the same track a second time or a new area of the disk,  $\mu_k$  was constant with sliding distance. For either of these conditions  $\mu_s$  was 0.18 and  $\mu_k$ , 0.10. Heating the disk did not alter the friction. The surface of this disk was then removed to a depth of 0.11 inch (thickness decreased by 22%) and the surface reabraded. Friction was measured both before and after reheating. Again the results were essentially the same as those obtained after the initial abrasion. It is concluded that there was a higher concentration of additive F in the surface of a freshly molded disk. At a small distance below the surface and extending to a depth of at least 0.11 inch, there was a lesser but still appreciable amount of additive.

Both the static and kinetic coefficients of friction were 0.27 on the molded surface of a disk containing 2 wt-% of additive G. This is in contrast to most of the other disks, which exhibited much lower values of  $\mu_k$ . Kinetic friction did not change with sliding distance, and neither  $\mu_s$  nor  $\mu_k$  varied with repeated traverses. Abrasion caused an increase in friction to values comparable to those of the pure copolymer. Heating the disk did not alter the friction.

A disk of the pure copolymer was prepared, and a film of additive F a few mils thick was deposited on the disk. Since additive F was applied from a Freon dispersion, the resulting coating was not a continuous film. Friction was very low ( $\mu_s = 0.15$ ,  $\mu_k = 0.04$ ) on this disk. Friction was again measured on the disk after abrasion and after heating. In every experiment, the friction was high and characterized by "stick-slip" motion, i.e., the same as with the pure copolymer disk. Evidently, films deposited on the surface were easily removed by abrasion and did not diffuse into the polymer.

### Polyvinyl Chloride

Disks of polyvinyl chloride were prepared in the same manner and under the same conditions as those of the copolymer of vinylidene chloride and vinyl chloride. Results obtained (see Table 6) with surface-active agent A or with plasticizer DOP added singly or together to the polyvinyl chloride were comparable to those obtained with the copolymer. Additive A increased the contact angles and decreased coefficients of friction of the freshly molded plastic. Contact angles were increased and coefficients of friction decreased by the addition of DOP but not to the same extent as caused by additive A. After the disks were abraded and then reheated, the low-friction adsorbed film was not restored on the disk containing DOP but was partially restored on the disks containing additive A. When both DOP plasticizer and additive A were used in the same disk, coefficients of friction were also decreased. Abrasion caused only a small increase in  $\mu_s$  and  $\mu_k$ ; however, after the abraded surfaces were reheated, no decrease in  $\mu_s$  and  $\mu_k$  resulted.

## Polymethyl Methacrylate

Disks of polymethyl methacrylate were molded at 300°F and 10,000 psi for four hours. Disks free from additives were clear and transparent; the others were white and translucent with many small patches of white opaque included material. The results of measurements on these disks are summarized in Table 7.

Coefficients of friction of the pure polymer were very high for all surface conditions, and sliding in the machine was always characterized by "stick-slip" motion. Addition of either additives B or C much reduced  $\mu_s$  and  $\mu_k$  but did not eliminate the "stick-slip" behavior. Nearly the same reduction in friction was obtained with either 2 or 4 wt-% of additive B. After these disks were abraded, there was an increase in  $\mu_k$  of the disk containing 2 wt-% of additive B, but there was no increase in the disk containing 4 wt-% of B. Except for the lower value of  $\mu_s$  of the molded surface, the disk containing 4 wt-% of additive C behaved like that containing 4 wt-% of additive B. Abrasion caused a small increase in  $\mu_s$  and  $\mu_k$  of the former combination, and there was some surface film regeneration when the disk was heated. Finally, a disk containing 2 wt-% of additive C plus 5 wt-% DOP was studied. Friction behavior of this disk did not differ greatly from that containing 4 wt-% of additive C. A small increase in friction occurred when the surface was abraded, but there was no further change when the surface was heated. Coefficients of friction of the reheated disks containing 4 wt-% additive B or 4 wt-% additive C or 2 wt-% additive C plus 5 wt-% DOP were comparable.

All additives caused some softening of the polymer. Higher contact angles were again always associated with lower coefficients of friction. Figure 1 shows graphically the relationship between the coefficient of friction and the cosine of the contact angle  $\theta$  for water and hexadecane. Each of the five points on the curve corresponds to the surface of one of the five disks in Table 7. Both  $\mu_s$  and  $\mu_k$  increase as the cosine of the contact angle increases, i.e., as the apparent work of adhesion,  $w = \gamma_{LV}(1 + \cos \theta)$ , of the liquid to the solid increases. This same relationship between friction and surface energy is shown for the vinylidene chloride-vinyl chloride copolymer and for polyvinyl chloride in Figs. 2 and 3, respectively.

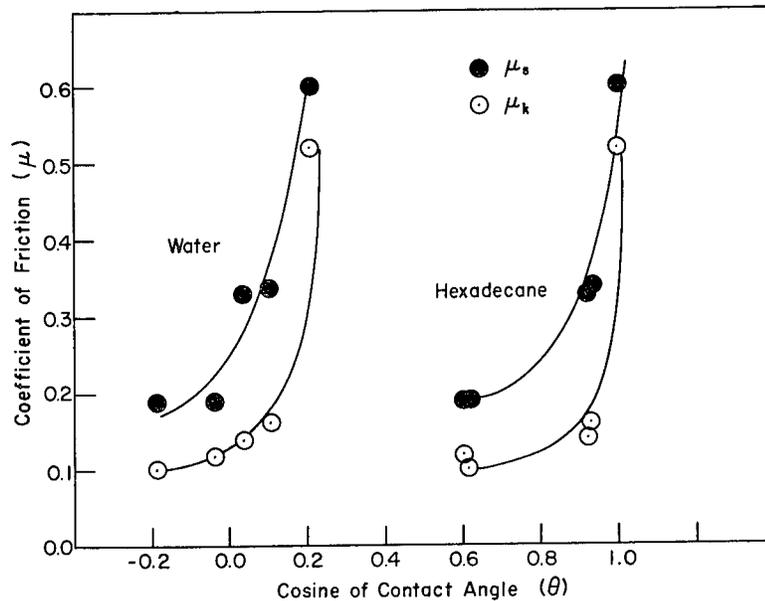


Fig. 1 - Relationship between friction and contact angle on polymethyl methacrylate

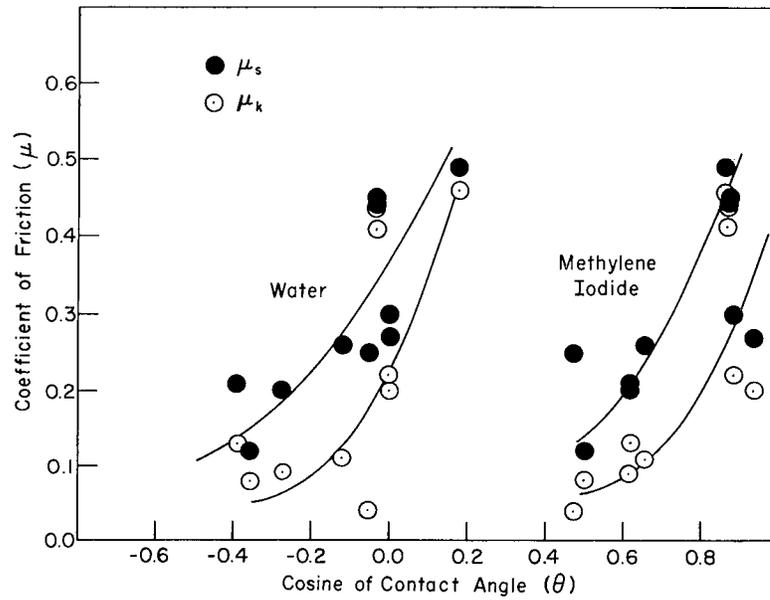


Fig. 2 - Cosine  $\theta$  vs  $\mu$  for vinylidene chloride-vinyl chloride copolymer

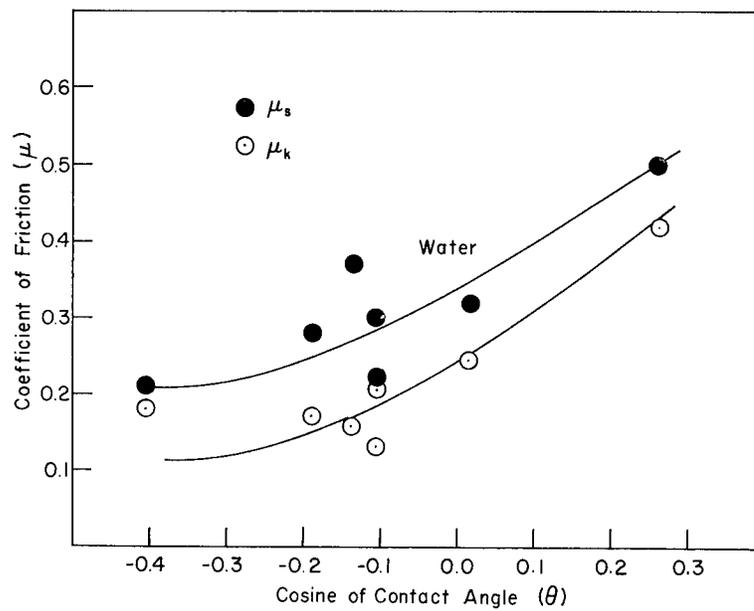


Fig. 3 - Cosine  $\theta$  vs  $\mu$  for polyvinyl chloride

## DISCUSSION

This investigation has shown that small amounts of appropriate fluorine-containing compounds can modify the friction properties of several polymers. These additives were effective in both polymer films prepared by evaporation from a solvent and in thick disks prepared from the melt. If a polymer can be considered as a liquid of very high viscosity, it should not matter how the additives are incorporated in the polymer, provided sufficient time is allowed for diffusion to the surface. The problems involved in selecting surface-active agents for polymeric systems should then be analogous to those of finding surface-active agents for any organic liquid. The presence of a high proportion of fluorine atoms in the additive molecule will not necessarily guarantee a low friction film, for the position of substitution is important. The effectiveness of a specific additive will depend upon its organophilic-organophobic balance with respect to the polymer. The percent of each additive found to be effective in these polymers is roughly equivalent to the amount needed to form saturated solutions in organic liquids containing the same polar groups (1,9-11) as the polymer.

The low-energy surfaces formed by the fluorinated additives may also be self-healing, that is, any surface-active molecule lost from the film may be replaced by the movement of additional material to the interface. The rate of self-healing will be accelerated by heating the polymer. Frictional heat could sometimes be sufficient to maintain a low surface-energy film.

The specific properties of the additives and polymers that control the rate of movement of additive molecules from the bulk polymer to the interface have not as yet been determined. One possibility would be that the rate of repair, or rate of surface regeneration, is a function of the glass-transition temperature ( $T_g$ ) of the polymer; that is, at temperatures below  $T_g$  the rate of migration would be very low, while at temperatures above  $T_g$  the rate would be much greater. However, in this investigation no correlation was observed between  $T_g$  and the temperature at which rapid repair of the surface film occurs. Reheating the disk at 50°C for four hours is sufficient to completely reform the film of additive A in polyvinylidene chloride, but no film is regenerated after many days at 25°C. Both temperatures are well above the glass-transition temperature (-17°C) for this polymer. With polyvinyl chloride the surface film again partially reforms at 50°C but not at 25°C; both temperatures are below the glass transition temperature (87°C). It is also possible that additive molecules will migrate to the surface through crevices or structural flaws in the polymer surfaces. Raising the polymer temperature may then increase the mobility of the fluorocarbon molecules and thus the rate at which they can move through the crevices and over the surface by surface diffusion or by vapor transport. The relation of the self-repair of these additive films to the imperfections and morphology of the polymeric solids is especially interesting; further research on this point is needed.

Many polymethylsiloxane derivatives would be expected to show surface activity in polymers having values of  $\gamma_c$  above 24 dynes/cm, while certain types of hydrocarbons and their derivatives will be surface active in those polymers having values of  $\gamma_c$  above 31 dynes/cm. The primary advantage of the appropriately designed fluorinated compounds, despite their greater unit cost, is that they will be effective in the lowest concentration and in polymers having the widest range of values of  $\gamma_c$ . They will also cause a greater decrease in friction and adhesion.

There are many promising applications of this technique to specific problems in lubrication and adhesion. Some suggested applications are the design or development of new plastic bearings or gears, the built-in reduction of friction and wear between synthetic fibers, the development of plastics in sheet form which will not self-adhere excessively when produced and shipped in rolls, and the preparation of plastics having decreased wettability by water, oils, or other organic liquids.

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13. ABSTRACT A new approach to the reduction of boundary friction in solid polymers has been studied. Dry frictional properties of several classes of polymeric solids have been reduced significantly by the addition of small proportions of a suitably designed surface-active compound. Appropriate fluorocarbon derivatives have been prepared and found effective in polymethyl methacrylate, polyvinyl chloride, and in several polyvinylidene chloride copolymers. These addition agents are effective both in polymer films prepared by evaporation from a solvent and in thick disks prepared from the melt. The low-energy surfaces formed by the fluorinated additives may also be self-healing, that is, any surface-active molecule lost from the film may be replaced by the diffusion of additional material to the interface.  The decrease in friction caused by the addition agent is accompanied by an increase in the equilibrium contact angle of each of several liquids on the polymer surface. The small proportion of addition agent used causes only a small decrease in the hardness of the polymers. There are many promising applications of this technique to specific problems in lubrication and adhesion.			

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