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Preparation and Wettability of Terminally Chlorophenyl-Substituted Carboxylic Acid Films

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ABSTRACT

Surface-active compounds can be designed to adsorb on solid surfaces to increase the adhesion of liquids, protective coatings, and resins. Often it is feasible to fulfill these requirements without necessitating a chemical reaction with both the adherend and adhesive. Various terminally substituted chlorophenylalkyl mono- and polycarboxylic acids were designed as potential adhesion promoters for certain classes of adherends. Methods were evolved for preparing an adsorbed monolayer of each compound by the melt retraction and other techniques. The wettability properties and the high critical surface tension obtained were consistent with values to be expected for such chlorine-rich surfaces. Moreover, the wettability proved insensitive to changes in homology and structure in these promoter molecules. Similarly, no changes in wettability were observed when the metal adherend was changed. The future implications of these results for improving the adhesion of protective coatings and adhesives were considered.

PROBLEM STATUS

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

AUTHORIZATION

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PREPARATION AND WETTABILITY OF TERMINALLY CHLOROPHENYL-SUBSTITUTED CARBOXYLIC ACID FILMS*

INTRODUCTION

In the past decade increasing attention has been given to improving adhesion in solid joints by designing "coupling agents" or "adhesion promoters." Some types are alleged to interact chemically with both the solid adherend surface and the polymeric adhesive. Coupling agents, such as the silanes (1) and certain coordination complexes of chromium (2), were introduced in the past decade to prevent loss of strength of glass-fiber-reinforced plastics during prolonged water immersion, i.e., to improve or promote wet strength. Such compounds have been alleged to function as coupling agents by compound formation with both adherend and adhesive, but there is much uncertainty yet as to the extent of compound formation, as well as the precise mechanism. Until recently, there was much debate about their value in improving wet strength (1) in composite materials.

Our understanding of the mechanism of adhesion and of the sources of weakness and failure in adhesive joints has increased greatly in the past decade, and increasing importance is being assigned to the wetting and spreading of the liquid adhesive for optimizing joint strength (3-5). An unanswered question is–to what extent is a chemical reaction at the joint interface <u>necessary</u> to promote formation of a strong joint? A related and important question is—must the coupling agent react chemically with <u>both</u> adhesive and adherend? Many physicists have long contended that intimate molecular contact of adhesive and adherend, without surface-chemical interaction, is sufficient to develop adequately high strength in adhesive joints.

But we must recognize that if the joint is subsequently to be exposed to occasional or long-term immersion in water, which may cause hydrolysis or corrosive attack, etc., surface-chemical reaction may be essential to prevent early joint failure. Therefore, chemisorbed coupling agents may be necessary for long joint life under water-immersion conditions. The question then arises—are the available agents the most suitable for all systems and uses? We think they are not. Several new classes of surface-active materials have, therefore, been designed and synthesized at NRL (6-8) as candidate adhesion promoters. We will present here progress of our current investigation of carboxylic acid derivatives containing terminal p-chlorophenyl substituents as suggested several years ago (5). The molecules of these materials were designed to be sufficiently surface active to chemisorb on the solid adherend surface; the adsorbed monolayer of the coupling agent was to present an outermost surface on which the liquid adhesive could spread spontaneously without chemically reacting with that film surface.

Since many organic adhesives and paints are applied as solutions or dispersions having low surface tensions, it might be supposed that they would, invariably, spread spontaneously on those adherends having high-energy surfaces and the use of an adhesion promoter to improve wetting would be unnecessary. Such a condition is usually not the case, however, because innumerable materials, as commonly applied, do not spread spontaneously on the many high-energy solid surfaces which quickly adsorb either water or undesirable organic contaminants. An important and unrecognized function of the

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adsorbed film of adhesion promoter is to prevent such contamination; hence, it can serve as a "priming" or preliminary protective coating for the high-energy solid surface during the period prior to application of the liquid adhesive or coating. A second and related function is to prevent the adsorption of undesirable contaminant materials that migrate toward the high-energy adherend surface from the liquid adhesive after it has been applied. In either case, a firmly bound adsorbed monolayer of the adhesion promoter will prevent or repress such contamination of the adherend surface by organic substances or by water, which could interfere with spontaneous spreading by the liquid adhesive, interpose a weakly bound layer at the interface, or introduce a plane of easy parting after solidification of the adhesive (3,4).

However, if the adsorbed film of the coupling agent is to serve well as a thin-film protective coating prior to application of the adhesive, the agent molecule should be designed to coat the adherend with an external surface having the following characteristics: (a) it should be sufficiently inert chemically; (b) it should have a low surface energy; (c) it should form a hydrophobic barrier film in order to avoid the accumulation of an outermost adsorbed layer of water, which could prevent the spontaneous spreading and good wetting by the organic liquid adhesive at the time of application (9), and possibly also serve as a plane of easy lateral migration of water molecules across the joint. Therefore, the film of the coupling agent should have a critical surface tension for spreading (γ_c) which is more than, or is only slightly below, the surface tension (γ_{LV}) of the liquid adhesive as it is applied. A value of γ_c of 32 dynes/cm would permit the organic liquids used in most common polymeric liquids and paint compositions to spread readily over the surface without void formation or excessive trapping of air bubbles. The result would then be to minimize the formation at the adhesive/adherend interface of regions where high stress concentration or a plane of easy cleavage or parting could develop (5).

Figure 1 presents, schematically, the role of a surface-active adhesion promoter in an adhesive joint. The desired wetting properties are obtained by incorporating an appropriately chosen atomic grouping at the outer end of the oriented adsorbed molecule. The opposite end of the molecule can comprise one or more polar groups, each of which is able to adsorb, as independently as possible, on the adherend surface either by strong physical or chemical adsorption. The coupling agent would thus be highly resistant to displacement by solvents or by surface-active components in the liquid adhesive. Since the small size of the water vapor molecule makes moisture permeation of organic coatings a constant threat to the integrity and longevity of adhesive joints, the coupling agent should be more hydrophobic in constitution than hydrophilic. Finally, where there is a chemical reaction between coupling agent and adherend, the product should have optimum water-immersion resistance by not being soluble in water and by being as resistant as possible to hydrolysis.

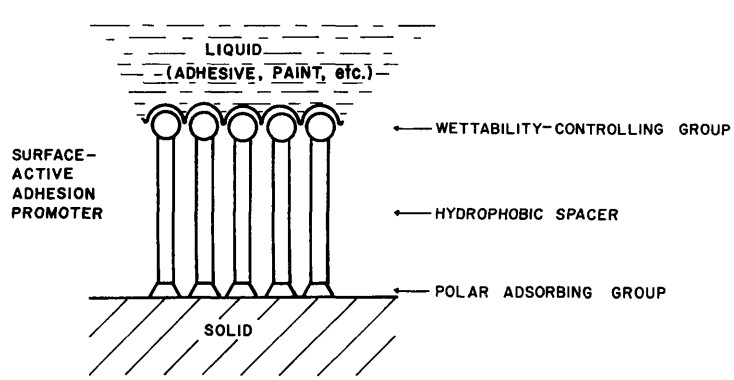

Fig. 1 - Schematic representation of a surface-active adhesion promoter

Coupling agents presently used in glass-fiber-reinforced plastics were designed to have an outermost exposed atomic grouping which is supposed to react chemically with molecules of the liquid adhesive by vinyl polymerization, for example. One common problem is that γ_c of an adsorbed monolayer of such a coupling agent is too low relative to the surface tension (γ_{LV}) of the liquid adhesive as it is being applied. Another problem is that the adherend surface can become contaminated before the coupling agent has been applied. If the coupling agent is applied in advance as a protective film, it must be designed properly to prevent the chemical reactivity of the outermost portion of that film from causing serious problems, such as: (a) lower oxidation or thermal stability, (b) ability to adsorb moisture, when in contact with either the atmosphere or the liquid adhesive, or (c) generation of reaction products which may be toxic, corrosive, or otherwise detrimental to joint strength. Item (c) is particularly important, since any harmful reaction products are concentrated within a few angstrom units of the joint interface.

An outermost chemical group having much appeal in a coupling agent is the p-chlorophenyl group (5). An adsorbed, closely packed monolayer containing such a group will present a surface which is rich in outermost covalently bonded chlorine atoms. Based on much previous research at NRL (10), chlorine-containing surfaces, such as adsorbed monolayers or polymeric solids, have surfaces which are very hydrophobic, are resistant to chlorine hydrolysis, and yet have critical surface tensions of wetting of 40 dynes/cm or more at 20° C. By attaching a sufficiently long aliphatic chain to the phenyl group, para to the chlorine atom, the chain can serve as a flexible hydrophobic spacer between the two extremes of the coupling molecule; hence, that molecule can adsorb in the desired monolayer configuration with the chlorophenyl group outermost and the carboxylic acid group (or groups) innermost. These considerations led us to prepare and investigate (6-8) the use of monomolecular layers of ω-(p-chlorophenyl)alkyl-substituted mono- and polycarboxylic acids as coupling agents. The use of two or more acid groups per molecule is interesting because of the resulting decrease in the tendency of heat or solvents to desorb the film. Moreover, carboxylic acid groups should be particularly effective in promoting adsorption and adhesion to basic surfaces, such as the hydroxyapatite constituent of teeth, many common oxide-coated metals, and various kinds of glasses and ceramics.

To ascertain whether these materials are effective as adhesion promoters and really do operate by the mechanisms discussed here, it was necessary to develop methods suitable for applying the compounds to the solid adherend surface as close-packed adsorbed monomolecular layers and prove that the resulting adsorbed monolayers have the molecular orientation needed to optimize spreading and wettability. These two topics are the subject of the present report. Research is in progress on (a) developing the most appropriate techniques for applying these materials in adhesive and coating investigations, (b) investigating the strength and water resistance of the resulting joints and protective coatings, and (c) comparing the results obtained with these and presently used coupling agents or adhesion promoters.

EXPERIMENTAL MATERIALS AND METHODS

The ω-(p-chlorophenyl)alkyl derivatives which were studied are listed in Table 1 by name, structural formula, and melting point. All three acids were white crystalline solids. The simple letter designation given in the first column will be used hereafter to identify each compound. All of these new compounds were synthesized, purified, and characterized at NRL by our associates, J. G. O'Rear, P. J. Sniegoski, and F. L. James (6-8). Each preparation was pure enough to be used by us as received. When it was necessary to apply the acid from solution, solvents were used which had been carefully purified by distillation and chromatographic adsorption.

Adsorption experiments were conducted on chromium, platinum, cadmium, and zinc; the sources and preparation of these metal specimens have been reported previously (11). In preparing adsorbed, monomolecular layers by adsorption directly from the molten pure acid (12), the clean adsorbing substrate was first heated to a temperature just above the melting point of the acid (see Table 1), a few crystals of the acid were sprinkled on the surface, and the resulting pool of molten acid was teased over the whole surface with a freshly flamed platinum wire. If spontaneous retraction of the liquid acid did not occur, the specimen was allowed to cool, and all of the solidified material adhering on top of the adsorbed monolayer was removed by appropriate solvent treatments as indicated below.

Table 1
Formulas and Melting Points of ω-(p-Chlorophenyl)alkyl-Substituted Carboxylic Acids

Identifying Symbol	Name	Formula	Melting Point (°C)
A	Monocarboxylic acids	$ClC_6H_4(CH_2)_nCOOH$	
	ω-(p-chlorophenyl)-dodecanoic acid	$ClC_6H_4(CH_2)_{11}COOH$	64-66
	Dicarboxylic acids	$ClC_6H_4(CH_2)_nCH(COOH)\ (CH_2)_{x-1}COOH$	
B	ω-(p-chlorophenyl)-dodecyl succinic acid	$ClC_6H_4(CH_2)_{12}CH(COOH)CH_2COOH$	87-88
C	2-ω-(p-chlorophenyl)-dodecyl glutaric acid	$ClC_6H_4(CH_2)_{12}CH(COOH)\ (CH_2)_2COOH$	85-86

The wettability of the acid film remaining on the metal was determined by measurements, at 20° C, of the angle of contact exhibited by sessile drops of a series of purified organic liquids whose source and methods of purification have been described by us elsewhere (13). Measurements with a direct reading goniometer telescope (13,14) were made by the drop profile method on the slowly advancing contact angle (θ) obtained by adding successive small increments of liquid to the sessile drop (3,4).

WETTABILITY OF MONOLAYERS OF ω-(p-CHLOROPHENYL)DODECYL GLUTARIC ACID ON CHROMIUM

The new compound, ω-(p-chlorophenyl)dodecyl glutaric acid (C in Table 1), is of particular interest as a coupling agent because it has two potentially active acid adsorbing groups at one end of the molecule. These carboxylic acid groups are separated by a hydrocarbon chain of sufficient flexibility to permit both groups to adsorb simultaneously on the adherend; therefore, the coupling agent should have an increased adsorptivity, as well as a decreased tendency to desorb when hot or exposed to solvents.

Emphasis was first placed on the adsorptive behavior of Compound C on the surface of chromium because that metal has the following desirable properties: (a) it is an excellent adsorbent for carboxylic acid groups (12); (b) a large body of data is available on the properties of adsorbed, monomolecular films of aliphatic (11), partially fluorinated (15), fully fluorinated (16), and chlorofluoro carboxylic acids (16); (c) the metal surface can be readily and reproducibly cleaned by standard metallographic polishing techniques; (d) there is a hard, coherent, thin-film oxide on the surface (17).

The "melt method" of applying the adsorbed monolayer was attempted first because the absence of solvent molecules prevents the competition for adsorption sites and the possibility of mixed film formation (18). In the past, when the melt method was used for the preparation of films of aliphatic or fluorinated acids, the molten acid spontaneously retracted because the surface tension (γ_{LV}) of the melt was sufficiently larger than the value of γ_c of the monolayer-coated surface (3,4,19). In the case of the chlorophenyl-substituted carboxylic acids, however, the difference between γ_{LV} and γ_c was not sufficient to promote liquid retraction; hence, the adsorbing surface always remained covered with the bulk acid, which coated it with a solidified layer as the specimen cooled. Therefore, to prove the existence of an underlying adsorbed, condensed, and adherent monomolecular layer of the coupling agent, it was necessary, first, to remove the surplus acid from the surface and, second, to measure various liquid contact angles on the coated surface after successive solvent treatments designed to remove any residual acid not firmly bound to the chromium surface.

Table 2 presents the results of some wettability measurements on adsorbed monolayers prepared from molten Compound C on pure, polished, and clean chromium surfaces after solvent treatment had been used to remove all surplus solidified acid. A series of successive solvent treatments was applied to each coated specimen (see first four columns of Table 2), using liquids which have been shown to be good solvents for Compound C in the bulk (8). These liquids were absolute ethyl alcohol or benzene at or above 20°C or n-hexane at or above 60°C. In the remaining columns are listed the average values of the slowly advancing contact angles, measured by the drop-buildup method on from three to five different drops. Measurements were made on sessile drops of water, thiodiglycol, and methylene iodide. These three "diagnostic" liquids were chosen because of their high surface tensions (72.8, 54.0, and 50.8 dynes/cm at 20°C, respectively) and because they differed greatly in molecular diameter (20) and hydrogen-bonding ability. The contact angles of Table 2 reveal, unequivocally, that the solvent treatment removed all of the visible coating of C, leaving behind a surface of the same reproducible wettability with respect to the three diagnostic liquids. The result was the same regardless of the choice of the solvent. As the residual adsorbed film was then found solvent-resistant (i.e., there were no further changes in wettability), it could be concluded that the residual film was only a monolayer thick.

In addition to the observations on the three diagnostic liquids required to establish the reproducibility of films formed from the melt, contact angle (θ) measurements (Table 3, last column) were made on several other liquids having surface tensions (γ_{LV}) ranging, at 20°C from 27.6 dynes/cm for n-hexadecane to 63.4 dynes/cm for glycerol. Figure 2 is a plot of cos θ versus γ_{LV} for the three diagnostic liquids, as well as ten other liquids. The majority of the data points fall within a narrow rectilinear band of approximately the same spread or width and location as were reported by Ellison and Zisman (10) for the chlorine-rich surface of smooth, clean, bulk poly(vinyl chloride). By analogy with their treatment of the data for that solid surface, we have used the intercept of the lower limb of the narrow band in Fig. 2 to assign the value γ_c = 39 dynes/cm for the adsorbed monolayer of Compound C. Complete spreading was observed with three hydrocarbon liquids (n-hexadecane, dicyclohexyl, and 1-methylnaphthalene) having surface tensions, at 20°C, less than 39 dynes/cm. The one exception to data points falling within the narrow band was ethylene glycol, whose contact angle was higher than would have been predicted on the basis of its surface tension, leading to one possible explanation that excessive moisture pickup from the air occurred during contact of the liquid with the monolayer-coated surface. No contact angle measurements have been reported previously for ethylene glycol on any other chlorine-rich surfaces to indicate whether this liquid also behaved abnormally on them.

Because of the potential application of Compound C as an adhesion promoter for protective coatings or for dental restorative systems, methods of preparing the monolayer

Table 2
Solvent Resistance of ω-(p-Chlorophenyl)dodecyl Glutaric Acid Monolayers on Chromium (Monolayer Prepared by the Melt Method*)

Successive Treatments on a Single Specimen				Advancing Contact Angles (in degrees) at 20° C		
Solvent	Temp (°C)	Treatment	Treatment Period (min)	Water	Thiodiglycol	Methylene Iodide
Specimen 1						
Ethanol	20	Rinse	5 (10 cc)	82	49	35
Specimen 2						
Ethanol	20	Rinse	1	81-1/2	49	36-1/2
Ethanol	20	Rinse	1	82	—	—
Ethanol	20	Immersion	15	82	—	—
Ethanol	78.5	Immersion (boiling)	15	81	48-1/2	36-1/2
Ethanol	—	Soxhlet extraction	15	81-1/2	48-1/2	36
Benzene	—	Soxhlet extraction	15	82	—	35
Specimen 3						
Benzene	20	Rinse	5	82	—	34-1/2
Benzene	20	Rinse	5	82	—	35
Benzene	20	Soxhlet extraction	15	83	—	34-1/2
Specimen 4						
n-Hexane	—	Soxhlet extraction	15	80	49	33-1/2
n-Hexane	—	Soxhlet extraction	15	79	—	—

*Each specimen was prepared by contact for 60 to 90 minutes with the molten acid at 90 to 96° C.

Table 3
Effect of Acid Structure on Wettability of Films from Melt *

Wetting Liquids	γ LV At 20°C (dyne/cm)	Contact Angles on		
		Chlorophenyl-dodecanoic Acid	Chlorophenyldodecyl Succinic Acid	Chlorophenyldodecyl Glutaric Acid
Water	72.8	81°	82°	82°
Glycerol	63.4			69
Formamide	58.2	70	70	67
Thiodiglycol	54.0	50	51	49
Methylene iodide	50.8	33	32	34
Ethylene glycol	47.7			57
sym-Tetrabromoethane	47.5	25	25	25
α-Bromonaphthalene	44.6	18	18	17
o-Dibromobenzene	42.0			12
Tricresyl phosphate	40.9			21
α-Methylnaphthalene	36.4			6
Dicyclohexyl	32.8	spread	spread	spread
Hexadecane	27.6	spread	spread	spread

*Films adsorbed on chromium during 1-hour contact with molten acid; solidified surplus acid removed with ethanol at 20° C.

were sought which would not require heating the adherend as much as required in the melt method but which would, nevertheless, result in reproducible adsorbed monolayers having the same desired molecular orientation and the closest possible molecular packing. The high γ_c of the monolayer formed by the melt method showed that it would be necessary to use solvents of high surface tension if spontaneous retraction was to be obtained for films formed by adsorption from solution. The theoretically and practically most obvious solvent to use was water. Unfortunately, Compound C is not soluble in water; even the addition of alkali to the water was of little help. Thus far, attempts to isolate the monolayer hydrophobically from aqueous solution have failed. An alternate approach would be to convert the water-insoluble acid into a more soluble form, such as a salt, and form the desired adsorbed monolayer from application of an aqueous solution of the salt at the most suitable pH for that solid substrate.

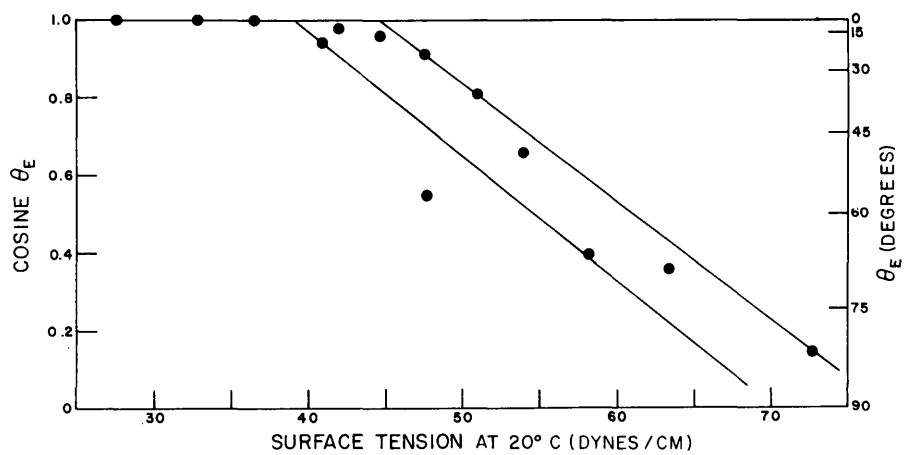

Fig.2 - Wettability of ω-(p-chlorophenyl)dodecyl glutaric acid monolayers adsorbed on chromium by the melt method

Greater success was achieved with mixed solvents, using a nonaqueous component which is miscible with water and is also a good solvent for Compound C. Solutions containing weight concentrations of C from 4×10^{-5} to 2×10^{-4} were tried using weight ratios of 1:7 to 11:1 of ethanol to water. The metal specimen was always immersed in each solution for 1 hour at 20°C. Partial or incomplete retraction on chromium was observed for all solutions except those with very high water contents (and consequently, high surface tensions). Complete retraction was observed for the 1:7 ratio; the surface tension corresponding to such an aqueous ethanol solution is 43.8 dynes/cm (21). Despite incompleteness of retraction from solutions containing lower proportions of water, contact angle measurements with distilled water on the retracted areas were all from 60° to 75°. These values are to be compared with the hydrophobic contact angle of 82°, characteristic of monolayers obtained by the melt method; they, therefore, indicate hydrophobic contact angles of 73% to 92% of the value characteristic of the most condensed monolayers. Such high surface coverages by the adsorbed film may prove adequate for many practical applications, since usually it will not be practicable to use the melt method, and treatment with an appropriate aqueous solution of Compound C may be more convenient.

Attempts to increase the contact angles of the diagnostic liquids by changing metal immersion conditions were not effective with the ethanol-water solutions. These attempts included: (a) increasing the concentration of C by a factor of as much as four, (b) prolonging the immersion period from 1 to 64 hours, or (c) raising the temperature of immersion from 20°C to 50°C.

When pure ethanol was used as the solvent for Compound C, no retraction of the solution was observed from a chromium surface immersed for 1 hour at 20°C. After evaporation of the solvent, the coated chromium surface exhibited hydrophobic contact angles ranging from 60° to 70°. However, contact angles of 80° were obtained after the chromium surface had been immersed in the same solution for 19 hours at 50°C.

Nitrobenzene is a fair solvent for Compound C and has a surface tension (43.3 dynes/cm) which is comparable to the γ_c of films of Compound C formed by the melt method. Dilute solutions of C in nitrobenzene in weight concentrations of 9×10^{-5} to 6×10^{-4} showed more limited retraction and lower contact angles than were obtained using films prepared by the melt method. Greater success in approximating the high contact angles of films formed from the melt resulted on subjecting the monolayer-coated chromium surface, after removal from the nitrobenzene solutions, to various surface treatments, i.e., to treatments after all molecules of C in the coating that were not packed in the monolayer had been removed.

A most significant result was that adsorbed films formed on chromium from the molten pure acid at elevated temperatures exhibited the same contact angle, regardless of the application of a variety of postadsorption treatments. These treatments included: (a) immersion in distilled water at 20°C from 1 to 16 hours, (b) immersion in distilled water at 100°C for 1 hour, and (c) exposure to steam in a closed system at 125°C for 1 hour.

Such immunity to postadsorptive treatment was not observed, however, with films of Compound C formed at 20°C by adsorption from organic or aqueous ethanol solution. As previously stated, such films, when initially prepared, exhibited uniformly lower contact angles than those prepared by the melt method. Following postadsorptive treatments, these coatings invariably showed increased contact angles. The treatments effective in increasing the contact angles included: (a) immersion in distilled water at 20°C, (b) prolonged rinsing with steaming distilled water, and (c) heating for 5 minutes in air at 70°C and 50% RH. In every instance the contact angle of the diagnostic liquid increased; about half of the postadsorptive treatments increased the contact angles to the values obtained by the melt method. In no case did the contact angle exceed the values observed for the same liquids on films from the melt. It is concluded that postadsorption exposure to moisture or heat, either singly or in combination, is very effective in increasing the contact angles exhibited by adsorbed monolayers of Compound C on chromium; hence, it should also increase the ability of the film to serve as a coupling agent. The effectiveness of heat treatment subsequent to adsorption in increasing the contact angle is consistent with the above observation that the contact angles for a film adsorbed from solution at elevated temperatures are high and approach those for a film adsorbed from the melt.

EFFECT OF CHANGING THE SOLID ADHEREND

In Table 4, contact angles and related data are presented to show the effects of changes in the solid adherend on the wettability of films of acid C adsorbed from the melt. The four metals reported here are arranged in order of increasing atomic radii (last column). Experimental values of the contact angles for each of the three diagnostic liquids were closely the same for all four metal adherends. Despite the considerable variation in chemical reactivity and atomic radii of the unoxidized metallic substrates, this finding is reasonable because this dicarboxylic acid molecule can not adlineate well on the surface in close packing, and the flexibility in the aliphatic glutaric acid chain allows the molecule to adsorb about as readily on metals having different metal lattice parameters. Several differences will be observed in the methylene iodide contact angles of Table 4. A value of 36°, which is not significantly different than the value given here for chromium, was observed with zinc, but there was a marked whitening of the underlying zinc and a decrease

in the hydrophobic contact angle from 80° to 50° in the surface area attacked. A significantly lower value of 29° was exhibited by methylene iodide on cadmium; however, there was no evidence of chemical attack of this metal surface.

Table 4
Effect of Metal Adherend on Wettability of ω-(p-Chlorophenyl)dodecyl Glutaric Acid Films from the Melt *

Substrate	Cleaning Procedure	Solvent for Removal of Surplus Acid	Contact Angles (degrees)			Atomic Radii of Metals**
			Water	Thiodiglycol	Methylene Iodide	
Chromium	Polished(11)	Benzene	82	50+	34	1.27
		Ethanol	82	49	35	
		n-Hexane(hot)	80	49	33	
Zinc	Polished(11)	Benzene	80	50	36***	1.38
		Ethanol	81		35***	
Platinum	Flamed foil	Ethanol	80	48	32	1.39
	Polished bulk material(11)	Ethanol	82	50	35	
Cadmium	Polished(11)	Benzene	82	51	29	1.54

* Films prepared on metal by contact for 60 to 90 minutes with molten acid at temperatures from 90 to 96 °C.
** R.T. Sanderson, "Chemical Periodicity," New York: Reinhold, 1960, p. 28.
*** Produced discoloration on surface which could not be removed by ethanol but could be eliminated by metallographic polishing. The discolored area showed a decrease in water contact angle to 50°.

In addition to film preparation by adsorption from the melt, Compound C was also adsorbed on pure platinum surfaces by adsorption from solution in nitrobenzene, ethanol, and ethanol-water solutions. As was true of films adsorbed on chromium, adsorption on platinum from solution resulted in surface coatings exhibiting lower contact angles than those formed from the molten acid. Postadsorption treatments were also effective in increasing the contact angles of films of Compound C on platinum.

EFFECT OF STRUCTURE AND HOMOLOGY

Research is still in progress on the effects of changes in the structures of these new types of acid adhesion promoters. Some interesting comparisons can be made between the mono- and dicarboxylic acids containing the same ω-(p-chlorophenyl) substituent attached through a long aliphatic chain.

The insensitivity of wettability to changes in the dicarboxylic acid portion of the molecule is revealed by comparison of the data in Table 3 for the substituted succinic acid (column four) and the substituted glutaric acid (column five).

Similarly, no significant change in wettability is observed when the dicarboxylic segment of the molecule is replaced by a single carboxyl group as in the case of the ω-(p-chlorophenyl)dodecanoic acid (column three), when prepared by the melt method. Monolayers of this same acid (Compound A) adsorbed on chromium from ethanol solution at 20° C exhibited lower hydrophobic contact angles (71° to 75°). Subsequent application of

moist heat to the surface films, however, resulted in wettability comparable to that for films formed from the melt (i.e., contact angles of 82°, 53°, and 37° for water, thiodiglycol, and methylene iodide, respectively).

The above data indicate that the packing of the terminal substituents in the close-packed monolayer is the same for both the mono- and dicarboxylic acids. This becomes understandable from consideration of the molecular models. In Fig. 3 the silhouettes of Stuart-Briegleb molecular models from Compounds A and C are shown. Both three-dimensional models were arranged to be as coplanar as possible so that differences in molecular cross-sectional areas could be judged from differences in their silhouettes in the plane containing the maximum number of carbon atoms. For both compounds this arrangement involved having the chlorophenyl substituent tilted with respect to the long axis of the extended aliphatic chain so that all phenyl carbon atoms could be in the same plane as the zigzag arrangement of aliphatic carbon atoms. A slight rotation toward the lower end of the alkyl chain would be sufficient in Compound C to bring the plane of the extended-chain glutaric acid moiety into coplanarity with most of the carbon atoms of the substituent in the 2-position. Such a rotation would increase the maximum dimension of the molecule perpendicular to the silhouette shown since the overall thickness of the chlorophenyl alkyl substituent is determined by the alkyl chain. This increase might be easily accommodated, however, in the relatively open space around the alkyl chain.

Figure 3 makes it apparent that the size of the chlorophenyl group limits the closeness of packing of the Compound A molecules if they adsorb in the configuration shown. In the case of Compound C, however, the limitation to close-packing in the plane of the projection is due to the glutaric acid moiety when in extended configuration. Closer packing might be attainable if the flexibility of the hydrocarbon chain between the two carboxylic acid groups facilitates their closer approach. Figure 3 also reveals that the differences in cross-sectional area between the chlorophenyl group and the glutaric acid moiety are not large; therefore, it is unlikely that the configuration of the latter can be deduced solely by contact angle considerations.

An interesting effect of varying the structure of the acids can be seen on comparing the behavior of films of two dicarboxylic acids differing in the length of chain between the acid groups. Studies in progress have found that films of the substituted succinic acid (Compound B), adsorbed on chromium after prolonged contact with dilute nitrobenzene solution, exhibited contact angles of 80°, 50°, and 32° for water, thiodiglycol, and methylene iodide, respectively. The closeness of these results to those reported above for Compound C is evident. Because of the difficulties already mentioned in preparing suitable solutions of Compounds A, B, and C in aqueous mixtures, the homologous acids having lower proportions of hydrophobic to hydrophilic substituents are under investigation and will be discussed in later reports. As predicted, the wettability of all these new acid

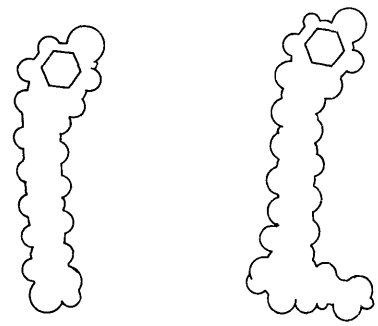

Fig. 3 - Silhouette of molecular models of Compound A and C in their extended configurations

coupling agents is determined by the chemical constitution of the exposed chlorophenyl group, with little or no effect on wettability arising from minor variations in packing density due to the nature of the polar adsorbing groups. The latter, however, may have a profound effect on the ease and strength of attachment of the adsorbed adhesion promoters on adherends of different physical and chemical properties.

CONCLUDING REMARKS

The results presented here prove that these new acid coupling agents do adsorb strongly on a variety of surfaces in the specific orientation (chlorine atoms outermost) which had been predicted (5) to be most useful for improving adhesion. In so doing they present an outermost surface specifically designed to have good wetting by most liquid adhesives, high resistance to oxidative or hydrolytic attack, and limited tendency to adsorb aqueous or organic contamination. The lack of retraction observed for the generating medium from the monolayer-coated surface is evidence of how well the adsorbed monolayer fulfills the requirement for good wetting by organic liquids. Moreover, the resistance of the monolayer to solvent extraction and washing treatments far more rigorous than those required to remove bulk acid provides evidence of how strongly adsorbed and resistant to removal these agent films are.

Research is continuing on new and more convenient modes of applying the acid agents and on the behavior of the agents on metals other than those reported here. Work also is in progress on certain nonmetallic surfaces which might be expected to interact with carboxylic acid coupling agents, such as certain types of glass, α-alumina, hydroxyapatite, certain ceramics, and some minerals.

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13. ABSTRACT

Surface-active compounds can be designed to adsorb on solid surfaces to increase the adhesion of liquids, protective coatings, and resins. Often it is feasible to fulfill these requirements without necessitating a chemical reaction with both the adherend and adhesive. Various terminally substituted chlorophenyl-alkyl mono- and polycarboxylic acids were designed as potential adhesion promoters for certain classes of adherends. Methods were evolved for preparing an adsorbed monolayer of each compound by the melt retraction and other techniques. The wettability properties and the high critical surface tension obtained were consistent with values to be expected for such chlorine-rich surfaces. Moreover, the wettability proved insensitive to changes in homology and structure in these promoter molecules. Similarly, no changes in wettability were observed when the metal adherend was changed. The future implications of these results for improving the adhesion of protective coatings and adhesives were considered.

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