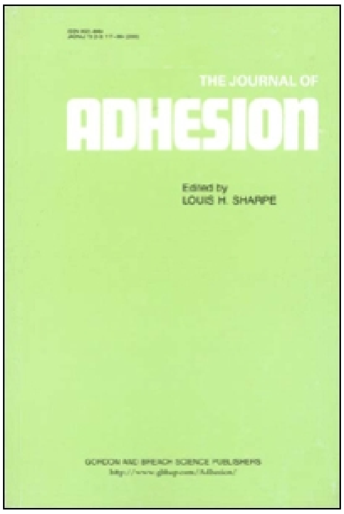

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Film Structure and Adhesion[†]

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Paint films although attached to a substrate on one side only may be subjected to stresses, comparable to those in structural adhesives. These stresses result from shrinkage during film formation and subsequent ageing, mechanical strains, relative thermal movements of film and substrate and from osmotic pressure due to soluble material under or within the film. The adhesive strength required to prevent detachment varies from very little for weak, highly porous coatings to 10,000 lb/in^2 for tough coatings of high elastic modulus. Generally, adhesive strength both to the substrate and between coats in a paint system must exceed cohesive strength, under the conditions when failure is likely to develop. Dispersion and other forces, such as hydrogen bridging, between coatings and clean metal substrates should suffice to ensure adhesion but most practical surfaces carry contaminants, which interfere with wetting and intimacy of contact. Solvents and other low molecular weight components may also provide a weak interfacial layer, at least for a period after application. Modification of polymer structure to improve contaminant displacement and to increase polymer/substrate interaction forces, for example by the introduction of polar substituent or end groups will be discussed and potentialities of adhesion-promoting surface treatments reviewed.

INTRODUCTION

In considering the adhesion of coatings to their substrates the significant question is not how do they adhere, but why should they detach? Unlike structural adhesives, which may unite massive components paint films are not usually heavily stressed by external forces. Indeed, often the weight of the film, usually in the range 1–50 mg/cm^2 is the only significant external force. It is not surprising that films of negligible cohesive strength, such as a chalk or grease pencil mark will remain on a surface, indefinitely, unless vigourously attacked. Why then do many coatings, including some of the toughest paint films, flake or peel from their substrates? The explanation

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appears to involve stresses generated in the coating, either during film formation or later through the effects of temperature change, water action or loss of volatile breakdown products.

STRESSES IN FILM FORMATION

Stresses arising during film formation will be considerd first. Until the development of solventless types, that were one hundred per cent film forming, all paints were applied with the aid of a volatile diluent, either water or an organic solvent.

With such materials, which still form the major volume of paints used, there occurs a continuous shrinkage of the applied film, due to solvent loss, throughout the period of conversion to a hard dry film and in some instances over a much longer period. Chemical curing processes also result in a compression of film structure, whether curing involves condensation, polymerisation or, as with drying oils, oxidation processes. As an extreme example the steady shrinkage of a long oil alkyd film over a month's period, measured by weighing the film under mercury is illustrated in Fig. 1.

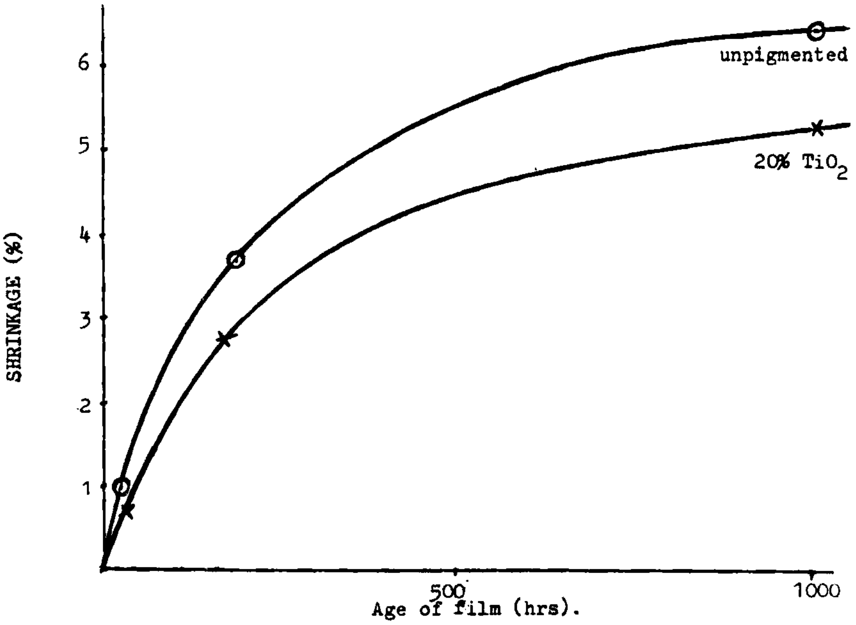

FIGURE 1 Shrinkage of alkyd films—aged at 25°C.

If shrinkage could occur without hindrance to the necessary rearrangement of the elements of the film structure stresses would not develop. However, in many films hindrance is significant, either on a macroscopic level, from interlocking pigment particles or, on a molecular level, from constraints of crosslinks or entanglement. A measure of the constraint on shrinkage can be obtained by detaching a dried film and taking it through a mild heating and cooling cycle in a dilatometer, when a relaxation in volume of as much as 5% is sometimes observed. The stresses that develop, as a result of these constraints, have been measured by a number of workers.[1,2,3,4] Thus Prosser, at the Paint Research Association, using a technique based on the curling of a steel shim, coated on one side only, measured a stress in a lightly plasticised (10% dibutyl phthalate) polymethyl methacrylate film (see Fig. 2) which built up steadily to about 75 kg. cm^{-2} after 10 days at 25°C. This film showed poorer adhesion than a more highly plasticised film (30% dibutyl phthalate) which developed an internal stress of only about 10 kg. cm^{-2}. If these stresses can be assumed tp be isotropic, to a rough approximation, they can be thought of as forces applied to the adhesive bonds at the substrate/film interface. In the most adverse cases it appears probable that forces

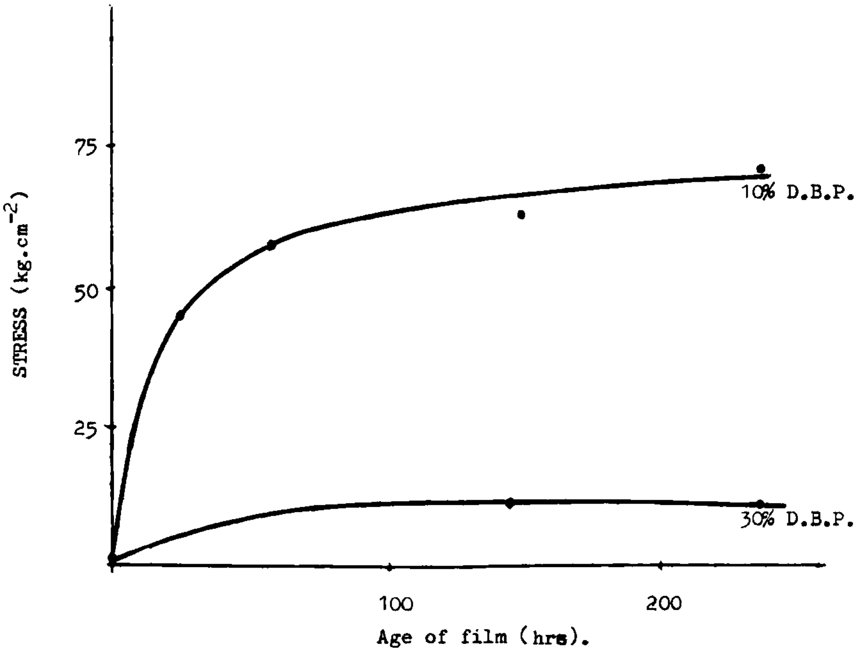

FIGURE 2 Internal stress development in plasticised polymethyl methacrylate films.

tending to break the adhesive bond, well in excess of 100 kg. cm^{-2} (1420 lb. in^{-2}) may develop. It is not surprising that spontaneous detachment sometimes occurs[5] or, where adhesion forces are strong, cracks develop in the film. The microcracking of etching primers based on polyvinyl butyral[6] is an example of this latter effect.

Even where neither detachment nor cracking results, internal stresses appear seriously to weaken adhesion. Thus Jakubowitsch and his co-workers[7] showed that when small proportions of plasticiser were added to polyvinyl chloride the force needed to strip films rose sharply as internal stresses fell.

Whilst the stresses set up as a result of constraints on movement during film formation are perhaps the most frequent cause of early adhesion failure other factors must also be considered. The more important are the effects of temperature and, especially, of water.

THERMAL STRESSES

Thermal expansion coefficients of paint films have been insufficiently studied. However, such data as are available indicate typical values below the glass transition temperature (T_g) of $3 - 8 \times 10^{-5}$/°C compared with $1 - 2 \times 10^{-5}$/°C for metals; above T_g the coefficients for paint films are two to three times greater. Thus cooling tends to induce greater contraction for a paint film than for a metal substrate. But a firmly bonded film cannot contract more than its substrate and so it is left under stress. Assuming a differential expansion coefficient of 5×10^{-5}/°C the maximum stress per unit cross-sectional area resulting from a 50°C fall in temperature is $2.5 \times 10^{-3} E$, where E is the elastic modulus of the film. Taking E as 5×10^{10} dynes. cm^{-2}, a typical figure for a highly cross-linked film, this stress becomes approximately 125 kg. cm^{-2}. For films of high elastic modulus, thermal stresses can indeed be large enough to exceed adhesion forces, resulting in detachment, or cohesive strength if this is lower, resulting in the form of cracking usually called "cold checking."

EFFECTS OF WATER

Water affects paint film adhesion in several ways, by swelling, by leaching out soluble components and thus causing shrinkage on drying out and by developing osmotic pressures when soluble material is trapped under a semi-permeable film. Water can sometimes have a useful plasticising function, in relieving stress, but more often the effects are deleterious. Swelling has been advanced as the cause of adhesion failure by blistering of paint films[8] but swelling would seem more likely to lead to rivelling, such as occurs when a solvent type paint remover is used on a cross-linked film. Certainly once adhesion failure has started at a crack, swelling forces may propagate the failure, causing peeling and flaking to occur. Blistering of paint films by water is mainly due to osmosis associated with soluble material under or in the films. Observations of the solute concentrations needed to suppress blistering indicate that osmotic pressures of at least 50 kg. cm^{-2} can be involved.

Several mechanisms by which stresses greater than 100 kg. cm^{-2} can develop in paint films have thus been identified. The magnitude of these stresses is related to environmental conditions and to bulk film structure and properties rather than to the nature of the interface between coating and substrate. In extreme conditions the stresses are comparable with cohesive strengths (ranging from 100 to 500 kg. cm^{-2} for the majority of organic coatings). Whether adhesion fails depends on the balance between these stresses and the adhesive forces that develop at the interface. The probability of failure can be reduced either by reducing stress development or by increasing adhesion forces.

FILM STRUCTURE AND INTERNAL STRESSES

Shrinkage stresses are large only if the coating gels to a solid film, with a significantly high modulus of elasticity, whilst a significant content of volatiles remains. Films formed from solutions of high molecular weight proteins, for example gelatin, which gel by intermolecular bridging processes can develop stresses sufficient to pull-off underlying dried paint films or even to crack glass substrates. Paints pigmented to the level where there is just sufficient non-volatile binder to fill the interstices between the pigment particles may also give high stresses, causing failure of underlying films.

To reduce stresses in high polymer solution films it is necessary to preserve intermolecular movements as late as possible during solvent loss, suitably by incorporation of plasticisers or proportions of solvents or coalescing agents of low volatility, that have a temporary plasticising effect. Another approach, in the organosol system, is to use a diluent with poor solvent power for the polymer so that the polymer molecules are not extended and do not entangle to form the equivalent of a cross-linked structure, before the diluent is lost. This latter technique will not give strong, adherent films from polymers that are rigid at room temperature unless the film is subsequently heated to permit interdiffusion of polymer molecules to occur. Heating also relaxes stresses formed during drying at room temperature, but it must be remembered that, with polymers of high T_g substantial thermal stresses may develop during subsequent cooling. This effect has been demonstrated by Holt, Bridge and Simpson who using a relaxometer technique,[2] even detected transition points by observing changes in the thermal coefficient of stress. However, the effect of simple heating treatments in improving adhesion of paints can be dramatic as is shown in Table I.

TABLE I

Effect of curing temperature on adhesion

	Joint strength (kg. cm^{-2})/area of adhesion failure %				
	Solvent wiped Al			Chromated Al	
Paint type	25°	120°	170°	120°	170°
Vinyl copolymer	0/100	99/100	269/0	163/0	
Vinyl copolymer with maleic acid	135/100	248/0	294/0		
Melamine/alkyd		128/100	160/75	334/0	424/0
Urea/alkyd		182/100	202/75	372/0	390/0

Another approach to the reduction of internal stresses in pigmented coatings is deliberately to induce microscopic fractures, for example, by the introduction of coarse lamellar or fibrous pigment, which will permit local stress relief. This technique, which may account for the excellent durability of micaceous iron oxide paints and some other thick film types, is somewhat analogous to the microcracking process for chromium plating.

ADHESION FORCES IN PAINT FILMS

The foregoing arguments indicate that the strength of adhesion forces needed to prevent detachment may be quite small for mechanically weak films, or films matching their substrates in thermal expansion coefficients and degree of swelling by water. The safe level of adhesion, however, must always be at least as high as the cohesive strength of the coating. With the toughest coatings cohesive strength can range as high as 700 kg. cm^{-2} (10,000 lb. in^{-2}) at least under high strain rate conditions. Whilst, for the majority of films the so-called dispersion forces between polymer molecules and clean metal oxide substrates should suffice for effective adhesion, stronger localised linkages, such as hydrogen bridges are probably necessary to give the required average bond strength on surfaces of industrial cleanliness. This is largely because these surfaces carry contaminants which interfere with intimacy of contact on the solid substrate and which themselves provide a weak layer or, as with fatty acid monolayers an interface of very low interfacial energy.[9,10] Thus, we were able to improve the adhesion of a urea-formaldehyde paint to steel which had initially been swabbed with xylene from 55 kg. cm^{-2} to over 225 kg. cm^{-2} by abrasion and solvent extraction treatments of the substrate only, and to improve the adhesion of an alkyd paint to commercial aluminium sheet from 154 kg. cm^{-2} to over 301 kg. cm^{-2} (cohesion failure of the paint) by chromic/sulphuric acid treatment. The painting of plastics of low surface free energy and the overcoating of some paint films presents special difficulties for similar reasons.

In practical painting situations it is necessary to consider not the ultimate adhesion force obtainable for a particular paint/substrate combination but how much can be obtained quickly with minimum surface preparation. These considerations have dominated the adhesion research projects at the Paint Research Association over the last several years. The aim has been to devise coating materials or pretreatments that will displace contaminants and will develop bonds to substrates at least as strong as the cohesive strength of the films. In this work we have used a simple pull-off adhesion technique (with a Hounsfield Tensometer) as the main test method and have given at least as much attention to the proportion of the test area with an apparent adhesion failure as to the value of the failing stress.

ADHESION OF DIFFERENT PAINT TYPES

Some generalisation can be drawn from the results of many tests over a long period. Thus the most consistent freedom from adhesion failure has been obtained with etch primers of the zinc chromate/polyvinyl butyral/phosphoric acid type. Very good results have also been obtained with high temperature cured thermosetting acrylics and amongst air-drying systems with polyurethanes cured with aliphatic isocyanates. At the opposite end of the scale, paints based on vinyl acetate/chloride copolymers have shown severe adhesion loss on all but the most carefully prepared surfaces and several other high polymer solution types have been little better. Paints based on vinyl copolymers containing 0.5 or 1% maleic acid in the chain have proved to be much more tolerant.

In a study of alkyd paints[9] it was found that polar fractions of low molecular weight were inimical to adhesion. However, adhesion, particularly to contaminated metal surfaces, appeared to depend on acid groups on the polymer, for methylation of carboxyl groups with diazo-methane noticeably reduced adhesion.

ADHESION PROMOTERS

Many attempts have been made to improve paint adhesion to industrial surfaces, either by pretreatment with solutions of so-called adhesion promoters or by incorporation of these materials in the paint. We concluded that an adhesion promoter must be of sufficiently small molecular size to be mobile and must contain groups able to compete satisfactorily with short chain fatty acids for adsorption sites on the substrate. After adsorption it was also necessary for reactive or polar groups to be exposed so that adhesion could be achieved between the promoter and the bulk of the film. Many materials fit this specification and promising results were obtained with, for example, sulphosalicyclic acid (3-hydroxy, 4-carboxy benzene sulphonic acid) and with some of the polyfunctional alkoxy silanes. Two difficulties were encountered. Adhesion promoters that were effective in unpigmented films were often of little value in pigmented systems presumably because the requirements for adsorption to a metal oxide substrate were similar to those for adsorption on inorganic pigment surfaces; in extreme cases bifunctional adhesion promoters caused gelation of paints. The second difficulty was that promoters that were effective in dry conditions lost strength under humid or water soaked conditions, the linkage either with the substrate or with the body of the film being attacked. Whilst the potentiality of this approach to the adhesion problem has yet to be fully explored it is believed that modification of actual film forming polymers is a more fruitful field of research.

MODIFICATION OF POLYMER STRUCTURE

Thermoplastic acrylic polymers were chosen as one of the simplest types amenable to controlled modification in the laboratory. Mr. R. A. Brett, in our first series of experiments, prepared a series of *n*-butyl methacrylate polymers modified with 1 to 5% molar amounts of acrylic acid, hydroxyethyl acrylate or acrylamide to introduce —COOH, —OH or —$CONH_2$ groups at intervals along the polymer chain. The polymers ranged in number average molecular weight, calculated from GPC data, from 79,000 to 152,000, the acid and hydroxyl values being in agreement with the formulations. Films were applied to aluminium treated in the following ways:

(1) degreased with trichlorethylene, acid washed and treated with sulphuric acid/dichromate

(2) cleaned to commercial level by trichlorethylene degreasing

(3) cleaned as in (1) and then contaminated by a solution of stearic acid in hexane at an application rate of 40 $\mu g.\ cm^{-2}$ of acid.

Films of unpigmented polymers were applied by spinning from toluene solution to give dried film thicknesses of 20 – 25 μm. Adhesion was measured using a Hounsfield Tensometer, joint strengths and area of adhesion failure being recorded (see Table 2).

TABLE 2

Adhesion of modified acrylic polymers to aluminium

	Joint strength (kg. cm^{-2})/area of adhesion failure %		
	Aluminium pretreatment		
Polymer modification	(1) Clean	(2) Commercial Cleaning	(2) Stearic acid contaminated
Nil	248/0	174/65	104/100
—COOH (1%)	299/0	200/100	125/100
—COOH (2%)	303/0	200/90	148/100
—COOH (5%)	342/0	250/20	196/100
—OH (1%)	192/0	161/90	93/100
—OH (5%)	260/0	174/85	107/100
—CONH$_2$ (1%)	216/0	196/55	98/100
—CONH$_2$ (3%)	206/0	192/45	131/100

Thus addition of carboxyl groups progressively improved adhesion without, however, achieving complete satisfaction on the deliberately contaminated surfaces; hydroxyl groups had no significant effect whilst amide groups gave only a minor improvement. Paints made with the copolymer containing 5% molar of carboxyl showed an even greater improvement in adhesion to contaminated surfaces as compared with the unmodified controls. Later experiments confirmed the marked improvement in adhesion to contaminated surfaces of paints based on the acid-containing copolymers but also demonstrated improvement of the unmodified polymers with pigmentation, probably because of reduced film shrinkage during drying.

In more recent work a much wider range of modifying monomers has been examined, particularly promising results being obtained with combinations of carboxyl and tertiary nitrogen groups in the polymer. All polymers examined so far show reduced adhesion on soaking in water for 48 hours, although adhesion is largely recovered on drying out.

SUMMARY

It has been shown that adhesion failure of coatings most often results from stresses developed within the coating. The magnitude of these stresses, and the ability to withstand them are determined by the structure of the film and the conditions under which it is formed. Specific adhesion forces between coating materials and clean substrates are relatively unimportant, except for the special case of painting over plastics of low surface free energy. However, on average industrial surfaces, that are difficult to free from contaminant, successful coating materials must incorporate groups that will compete favourably for adsorption sites with the contaminant. Carboxyl groups at molar percentages of the order of 1 % of the monomer are effective in securing adhesion to most contaminated surfaces but not wholly in maintaining adhesion under water-soaked conditions.

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