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BLISTERING OF PAINT LAYERS

AS AN EFFECT OF

SWELLING BY WATER

by

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Summary

An attempt is made to explain the occurrence of blisters in paint layers as an effect of two causes, *viz.* volume increase by swelling by water, and loss of adhesion. It is explained that this latter phenomenon is caused by the softening of the paint material and, therefore, is also indirectly an effect of swelling. The degree of swelling depends on the alkalinity of the water. In pure water the swelling of an unpigmented medium is so low that blistering cannot occur. Pigments, especially those which have an alkaline character, can increase the degree of swelling so that blisters may be formed. Means for preventing blistering are discussed.

INTRODUCTION

If a paint layer which is attached to any substrate, e.g, wood, steel or glass, blisters, one can be certain that there was contact with a liquid for a period of time. In practice, this liquid is usually water, however, water need not always be present to cause blistering. Many other liquids, e.g. alcohols, ketones and phenols can cause blistering and many of them in a much shorter time than water, for example, a few drops of acetone, placed on a paint or varnish layer can give heavy blisters almost instantaneously. However, as a general rule, blistering only occurs when the paint layer is in prolonged contact with a liquid. The reverse of this rule is not always true, and not every liquid will give blistering ; contact with a liquid is a necessary, but not a sufficient, condition for blistering.

Blistering means that the surface of the paint is increased ; what at first was the surface of a disc, grows out to form a segment of a sphere with the original disc as a base. This means an increase in surface area and also an increase of the volume of the paint film, if its thickness is not reduced. Reduction in thickness would imply that the film was in a stressed state and that the liquid or gas in the interior of the blister was under hydrostatic pressure. However, there is no evidence for such a situation. Neither in the interior of the blisters caused by water, nor in those brought about by other liquids, can it be proved that there is pressure as any liquid in the interior does not come out on pricking a blister. The fact that there is pressure in blisters originated from the idea that large forces would be needed to lift the paint layer from its substrate. This is a mistake, the same reaction between the liquid and the paint layer which causes blisters is also responsible for a loss of adhesion, for a paint layer soaked for a long time in water can lose its adhesion, not only under the blisters but everywhere else ; the layer as a whole lying loosely on its substrate. In this respect the behaviour of paint is no different from many other polymers. A stamp stuck on an envelope cannot be removed from the paper without damaging both the stamp and the envelope. Nevertheless, dipping the envelope for a short time in water is sufficient for a total loss of adhesion. Blistering is always connected with loss of adhesion, and no force at all is necessary to lift the paint layer.

Erroneously, osmotic pressure has been believed to be responsible for blistering. However, we have seen that pressure is not at all necessary for the phenomenon to occur. Moreover, a clear picture of the osmotic cell would have to be developed.

Two phenomena are characteristic of a blistering paint layer : (*i*) increase of volume, that is, swelling, and (*ii*) loss of adhesion. An explanation of blistering will be given by using these simple physical phenomena, also whether all the observed facts can be accounted for without any trouble by the concept of a polymer swelling by low molecular agents will be considered.

SWELLING

In general a low molecular weight liquid in contact with a polymer will penetrate through the polymer as a consequence of the increase in entropy caused by mixing. Molecular forces can contribute to the mixing effect, but there are also cases where they prevent swelling almost entirely. The rate of diffusion strongly depends on the temperature, but the solvent regained when the equilibrium is finally reached, depends only on the relative humidity.

The following is restricted to swelling by water only

Swelling of a paint vehicle is not caused by liquid water exclusively, but also by water vapour. Fig. 1 gives an idea of the rate of absorption. The water regained per cent by weight is here plotted against the logarithm of the time
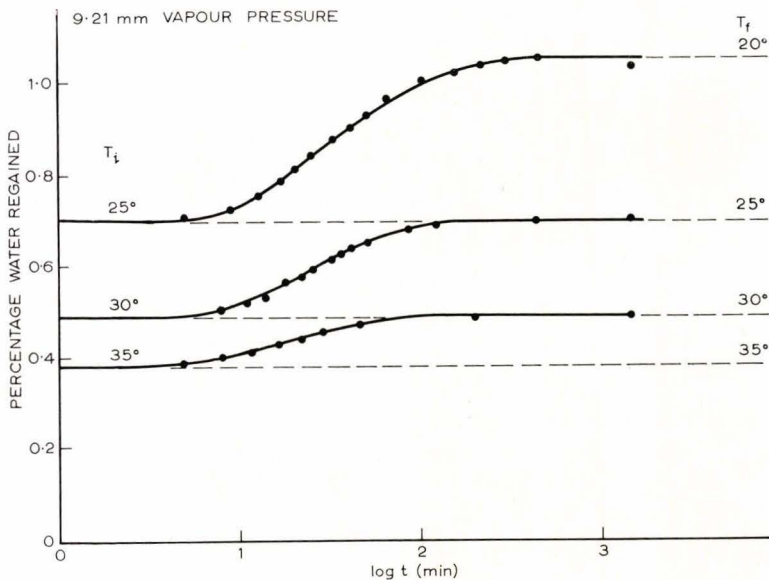

FIG. 1

Water absorption of an alkyd resin film at decreasing temperature and constant vapour pressure as a function of time. Abscissa : logarithm of time elapsed after a sudden decrease of temperature. Ordinate : water concentration in weight per cent of the dry specimen. Initial and final temperatures : T_i and T_f are chosen as indicated

in minutes since a sudden change occurred in the conditions, i.e., in the experiments described in Fig. 1, a decrease of the temperature whilst the vapour pressure remained constant. The lower the temperature the higher the equilibrium water regain. It can be seen that after a sudden decrease of temperature from 35 °C to 30 °C, about 70 minutes are necessary to achieve the new equilibrium. At 25 °C diffusion goes on much more slowly, and at 20 °C it takes more than 500 minutes to establish the new equilibrium. The experiment was carried out with a strip of film of an air-dried alkyd resin, with a thickness of 10 microns.

It follows from the theory of diffusion that

$$\frac{Q_t}{Q_e} = \frac{c\sqrt{t}}{d} \quad \text{(for } Q_t/Q_e < 0.6\text{)}$$

Q_t being the water regain at time t, Q_e the equilibrium water regain, d the thickness of the paint layer and c a constant. Thus an increase of d by a factor n requires an increase of t by a factor n^2 to keep the quotient Q_t/Q_e constant. For a film thickness of 40 microns the time interval mentioned above for a 10 micron film must be multiplied by 16. That means that swelling by water is a very slow process. At room temperature and with layers of the ordinary thickness it can take a few days for equilibrium to be reached.

From investigations published elsewhere[2] it appears that the water regained in the equilibrium state depends merely on the relative humidity and is independent of the temperature. In Fig. 2 the percentage weight of absorbed water
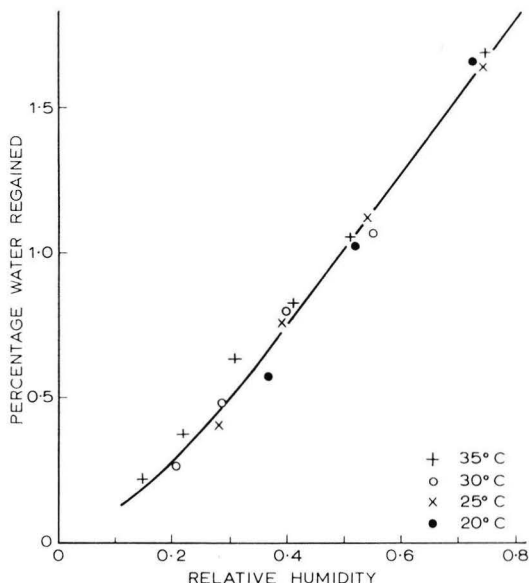

FIG. 2

Water concentration in the specimen as a function of the relative humidity. Abscissa : relative humidity, ordinate : water concentration in weight per cent of the dry specimen

is plotted against the relative humidity for various temperatures. It is clear that the relation between relative humidity and degree of swelling for all temperatures is the same. Of course, the rate of approaching the equilibrium state very much depends on the temperature.

Saturated water vapour must have exactly the same effect as liquid water, as can be concluded from some simple thermodynamic reasoning. If in a closed vessel a sample of the polymer, water and saturated water vapour are in contact with each other, and equilibrium is established, then the water regained by the polymer must be equal all over the film otherwise there would be a water " gradient " in the sample from places with higher concentrations to those with lower concentrations, this, however, is inconsistent with the system being in equilibrium.

For an air-drying alkyd resin the water regained in contact with liquid water or saturated vapour in the equilibrium state is at any temperature about 2.5 per cent by weight. However what is really of interest is the volume increase of the resin and not the weight of absorbed water. The question arises is an increase in weight accompanied by a volume increase of the same value. In general, the answer must be no, for as is well known, mixing 50 ml of alcohol and 50 ml of water does not result in 100 ml of mixture, but in a smaller volume. The question of volume increase and absorption was investigated for an air-drying alkyd resin. The results summarised in Fig. 3 show that the volume increase of the resin initially exceeds the proper volume of the absorbed quantity of water by a small amount, but for greater quantities the difference
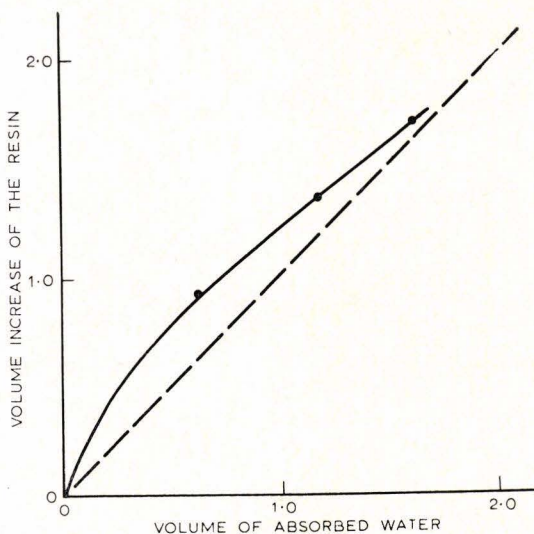

FIG. 3

Volume of the specimen as a function of the degree of swelling at a constant temperature of 20°C. Abscissa: the absorbed quantity of water expressed in volume per cent of the dry specimen. Ordinate : Volume expansion expressed by length increase as a fraction of original length (linear coefficient of swelling) multiplied by 3×10^2. (Volume swelling in per cent)

between weight percentage and volume percentage of absorbed water is negligible.

ADHESION

The very concept of adhesion is generally connected with some particular experiment or practical test ; one tries to strip off the polymer layer from its substrate and one estimates the force necessary to perform this action. This force is termed "adhesion". Unfortunately, it is only this experiment which is borne in mind, and which defines the notion of adhesion. This experiment, however, cannot be performed in reality, for a paint layer cannot be peeled from its substrate without damaging the paint film. Furthermore the experiment itself is not reproducible, as is frequently believed.

There are two reasons why adhesion experiments, undertaken in the ordinary way and nearly always from the viewpoint of testing, are doomed to failure ; (*i*) they are performed under ordinary laboratory conditions, and the investigators disregard the influence of temperature and (*ii*) the investigators neglect the proper time scale of the disruption process. A paint layer renowned for its excellent adhesion can be stripped from its substrate without difficulty if the temperature is raised to such a value that the paint is in, or below its transition region, and if the stripping is performed slowly. That is to say, the stripping force will be small if the paint material is weak and the rate of detachment is low. It all depends on the mechanical properties of the polymer.

The cause and effects of this phenomenon, can be illustrated by the model represented in Fig. 4. The substrate is shown by a horizontal line and a row of atoms of the adhesive is attached to it by very thin wires, representing the molecular adhesion forces working over very short distances. The wires can break, but they cannot be strained. Under the row of atoms making contact with the substrate is the mass of the polymer represented by a network of springs. Under these springs is the load, that is the stripping force, represented by small spheres. Two essentially different cases have to be distinguished here : (*i*) when the temperature is below the transition point, and the network then consists of stiff elastic springs, the stiffness being of the same order as the stiffness of the wires representing the molecular forces. (*ii*) When the temperature is above the transition point, and the network consists of weak " entropy springs " with a modulus which is a 1,000 times smaller than it is in the first case. Supposing, in both cases, the stripping force to be equal, then the stored elastic energy (being inversely proportional to the modulus) in this second case is also 1,000 times greater than in the first.

Let us now consider one of the atoms of the adhesive (the paint layer) in contact with the substrate. In Fig. 5 the distance from the atom to the substrate is plotted as the abscissa and the value of the force working on the atom as the ordinate. The molecular force field can be represented by the line ABC. The equilibrium position of the atom is at the point of intersection of this line with the abscissa. If it moves towards the substrate, it is subjected to a strong repulsive force increasing as the distance to the substrate diminishes. If the atom moves away from the substrate, there is at first an attractive force, increasing strongly with the distance, as far as point B, when the force gradually decreases and finally becomes zero at point C.
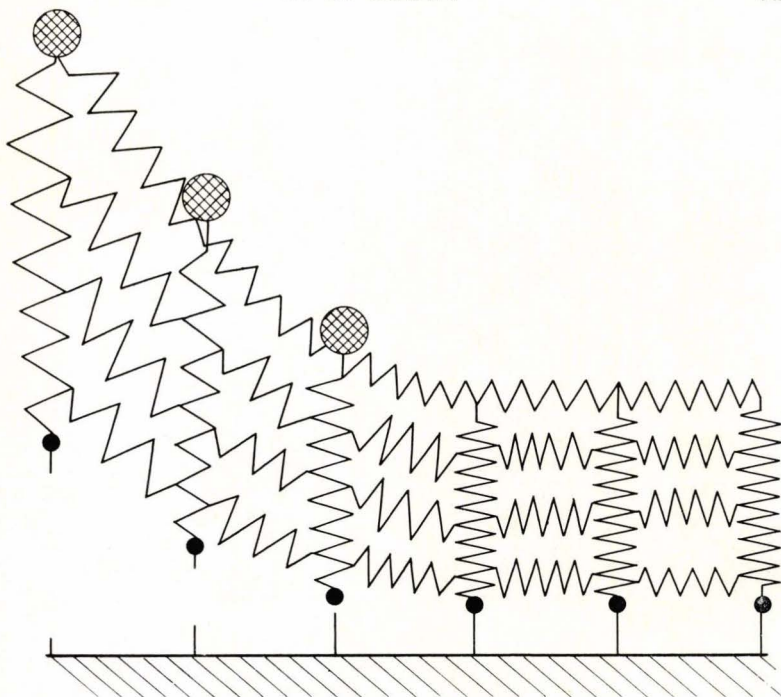
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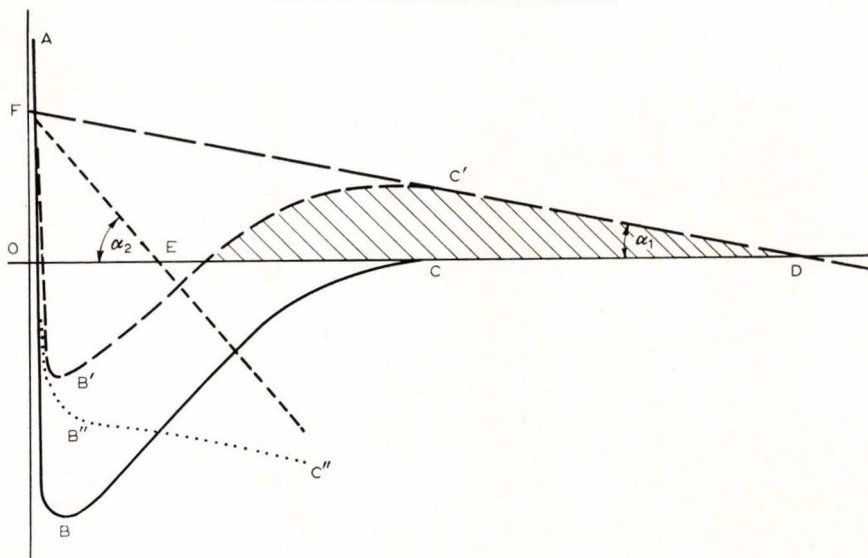FIG. 4. Schematic model of adhesion

FIG. 5. The forces to which an atom of the adhesive in the boundary layer is subjected. Abscissa : distance of the atom from the substrate. Ordinate : force acting on the atom

Superimposed on this molecular force field there is an elastic field resulting from the stripping force ; for simplicity, let us suppose this force to be Hookean. It is represented by the broken line *FD*, and the elastic modulus is given by *tan α D* in the equilibrium position that the atom would occupy, if the molecular force field were absent and all neighbouring atoms kept their places. The molecular and the elastic field together result in curve *AB'C'D*. It appears that there is now a large region (the shaded area) where the force is repulsive. There are two equilibrium positions the original one and *D*, and if the atom under the influence of the thermal oscillations can surmount attractive force *OB'*, it will jump to the new equilibrium position *D*, which means that it is detached. Considering that the frequency of the thermal oscillations are of the order of 10^{13} per sec., we must allow for the possibility that attaching and detaching occur continuously, many times per second. Although the stripping force *OF* is smaller than the adhesion force *OB*, nevertheless there will be an increasing detachment of the paint layer from its substrate under the influence of the thermal movement and the rate of this detachment, at a constant load, will be temperature-dependent.

Consider the first case in which the temperature is such that the polymer is below its transition region and the modulus of elasticity is high. It is assumed that the stripping force is equal to that of the second case *OF*, but the line of the elastic force field is now given by dotted line FEC. The elastic modulus *tan α₂* is greater than in the second case. The resultant force field is given by the dotted line *AB"C"*. This line is quite different from the second one. There is no longer a region of repulsive forces, a second equilibrium position does not exist and oscillations between equilibria under the influence of the thermal agitation cannot occur. As long as *OF* is smaller than *OB*, there will always be attachment ; but if *OF* increases and exceeds *OB* there will immediately be detachment. Thus there are two essentially different cases : (*i*) above the transition point where there is a low rate of detachment and temperature-dependent detachment which occurs with only small stripping forces, and (*ii*) below the transition point nothing occurs with small stripping forces, but with stripping forces exceeding a critical value there will be a sudden detachment at high rate (velocity of sound) and it will be temperature-independent.

There are many hard and brittle polymers which cannot be brought into the rubbery state by temperature increase, because chemical deterioration occurs long before the transition temperature is reached. There is, however, another way to decrease the modulus, namely through swelling. By swelling we pass from the first to the second case, from below to above the transition point. This explains why nearly all glues lose their sticking power when exposed to water or moisture. Of course, the real adhesive forces remain exactly as before ; nevertheless, it is seen that above the transition point detachment occurs with much smaller stripping forces. In the first case (below the transition point), adhesion is a balance of forces, and in the second case (above the transition point), it is a balance of energies. For further details reference should be made to another paper[2].

BLISTERING

The preceding arguments show that soaking a paint layer in water has two effects : (*i*) swelling, i.e. an increase of volume, and (*ii*) loss of adhesion, which

means that the force necessary for the detaching of the film from its substrate is strongly diminished. The picture of blistering that then suggests itself is that the volume increase leads to a weak stress in the film which tries to lift the layer from its substrate ; this results in a blister and in elimination of the stress. This explanation of the mechanism of blistering might explain the facts that are observed in practice.

Linear Coefficient of Swelling
This can be defined as the increase in length of the edge of a unit cube from the dry to the wet state. The volume coefficient is three times the linear one.

What is the connection between the linear coefficient of swelling and the dimensions of a blister ? Let us call the height of a blister h and the radius of the base r (Fig. 6). Then a piece of a paint film with an original area πr^2 has changed its area to $\pi(r^2+h^2)$. The factor of increase therefore is :

$$\pi(r^2+h^2) \ /\pi r^2 \ = \ 1+(h/r)^2$$

Thus if an area of 1 cm² changes to an area of $(1+\lambda)^2$ and if λ^2 is small compared with λ the expression reduces to $1+2\lambda$ Then

$$1+ \left(\frac{h}{r}\right)^2 \ = \ 1+2\lambda$$

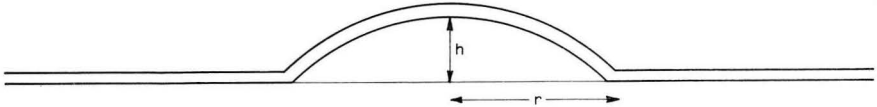$$\therefore \ \frac{h}{r} \ = \ \sqrt{2\lambda}$$

FIG. 6

Surface increase of a paint film due to blistering

The ratio h/r for most blisters amounts to about 1/5 ; only very few blisters have a smaller ratio.   The blister ratio 1/5 corresponds to a value of 1/50 for λ, and it must be concluded that a linear swelling ratio of about 2 per cent is a minimum condition for blister formation.

A simple method for measuring the swelling is as follows. From a free (detached) paint film, a small triangular shaped piece with edges of about 1/2 mm. is cut, using a sharp razor blade. This piece is placed on a microscope slide and the dimensions measured under small magnification with the aid of a micrometer eyepiece. A drop of water is then placed on the specimen and the whole is covered with a cover glass. At regular intervals the length of the edges is measured until equilibrium is reached. For a dried alkyd resin we have found the swelling ratios are as given in Table I.

TABLE I

LINEAR SWELLING PERCENTAGE OF AN AIR DRIED ALKYD RESIN FILM FOR VARIOUS
SWELLING AGENTS

AGENT	Percentage linear swelling
Acetone	30
50 per cent acetone + 50 per cent water	5
25 per cent acetone + 75 per cent water	1
Water	$\frac{3}{4}$
Alcohol	10
Aqueous saturated phenol	12
Aqueous saturated menthol	15
Benzaldehyde	26
Aqueous camphor	8

Table I shows that various organic liquids, especially ketones and aldehydes, can give considerable swelling of an alkyd resin. The figures refer only to the equilibrium state, and give no information about the time necessary for attaining equilibrium. For acetone the swelling was finished within a few seconds ; for benzaldehyde it required several days.

The swelling caused by water is so small that blistering cannot occur. This is in agreement with the fact that blisters in an unpigmented varnish are seldom observed. Table II gives the swelling percentage for some paints.

TABLE II

	Percentage swelling
Clear alkyd resin	0.75
Alkyd resin + lead titanate	2
Alkyd resin + titanium dioxide	3.5
Alkyd resin + zinc oxide	11

Table II shows that pigmented paints may swell to such a degree that blistering is possible, and that, for instance, a paint with zinc oxide can give heavy blisters. Although a paint may have been proved to be susceptible to blistering it does not necessarily mean it will blister in practice. The conditions for blistering may be summarised as follows :

(*i*) The paint layer must be soaked with liquid water or saturated water vapour, because for a relative humidity below 100 per cent the percentage of swelling is so much lower that no blisters can be formed.

(*ii*) Swelling is a very slow process. For a film with a thickness of about 40 microns it takes several days before equilibrium is reached. Therefore, a necessary condition for blistering is uninterrupted contact of the paint with liquid water for several days.

(*iii*) Swelling is a diffusion process and its rate depends on the temperature. Therefore, low temperatures will retard the formation of blisters.

In practice, all these conditions are not satisfied at the same time. For example, it is very exceptional for there to be uninterrupted rain for more than one day. But swelling is reversible ; if the rain is followed by dry weather, or wind, the swelling that has just started will reverse. On a painted structure there will only be few places where conditions (i) and (ii) are satisfied. Such places are horizontal grooves where water collects, the space behind raised rims, etc. on wood the conditions will be satisfied if the water comes from the inside of the wood, as it is quite immaterial from which side the water comes. Blistering can also occur on painted steel, and then the water, of course, enters the paint through the top layer. The idea that water can give blistering only when it comes from the inside of the wood is, therefore, false; it is connected with the deceptive picture of a high pressure being necessary to lift the film. There is, however, another reason why blistering occurs especially on wood. Often it is only in those cases where the water comes from the inside of the wood that the paint layer is soaked for long enough to cause blisters.

At first sight it seems enigmatical that pigmentation of a resin so much increases the swelling power ; for example, by a factor of 15 in the case of zinc oxide. In point of fact it is not the pigment itself that has this effect. The strong swelling in all these cases is caused by a change in the acidity of the water. Saying that the coefficient of swelling for an alkyd resin amounts to $\frac{3}{4}$ per cent is only justified if the pH of the water is about 7. If the pH of the water is 9, the swelling coefficient increases to 6 per cent. For a pH of 5 the swelling is negative, that is the resin material shrinks. The pigment changes the acidity of the water, especially the more basic pigments such as zinc oxide It is possible, at least in principle, to calcine pigments so that the surface of the particles becomes inactive. This is achieved by heating the pigment for a few hours at about 100°C below its melting point. The activity of the pigment is due to irregularities and micro-cracks in the surface, and it is much lower for ideal crystals. Table III gives, for some pigments, the influence of such calcining.

TABLE III

COEFFICIENT OF SWELLING FOR SOME PAINT FILMS IN DISTILLED WATER

	Percentage swelling
Clear alkyd resin	0.75
Alkyd resin+titanium dioxide	2
Alkyd resin+calcined titanium oxide	0.7
Alkyd resin+chromium oxide	5
Alkyd resin+calcined chromium oxide	1

However, the process of calcining can have an unfavourable influence on other properties such as hiding power and particle size.

Sensitivity to the acidity of the swelling agent is a property common to many polymers in fact, these polymers contain polar groups. These polymers can all swell under alkaline, and shrink under acid, conditions. It has been proposed to use such substances as synthetic muscle for they can convert chemical energy (alkali/acid neutralization) directly into mechanical energy (dilatation and contraction).

It is particularly the process of oxidative drying of an alkyd resin which produces many polar groups, and the acid number of a resin after drying is high. By contrast, polymers of the polyethylene type cannot swell at all in water, irrespective of the alkalinity, because they have no polar groups.

OTHER FACTORS WHICH AFFECT BLISTERING

The conclusion reached is that blistering can only be expected in those cases where a paint layer is in contact with liquid water for a long time (several days) uninterruptedly, when the temperature is not too low, when the medium has a polar character and the pigment has an alkaline reaction. It must be borne in mind that, in general, pigments are not chemically pure substances, and some can have additives which produce an alkaline reaction with water.

But even if all the above conditions are satisfied, we cannot be sure that blisters will be formed. Blistering is a result of two causes : swelling and loss of adhesion. The lifting of the paint layer is realised by a continuous process of detachment which consists essentially in the propagation of a tear between the paint layer and its substrate. It is likely that the tear starts at one or another small irregularity on the surface of the substrate, such as a dust particle. If the substrate is not flat, the stress in the film results in a force directed upwards on the tops of the elevations and downwards in the centres of the depressions (Fig. 7) ; rows of blisters can often be observed along the top of ridges on wood. Another cause for blistering in a certain place may be the swelling of the wood itself, which may be asymmetric. Sometimes blisters on wood are oblong, which certainly is an effect of the combined action of swelling of the wood and of the paint.
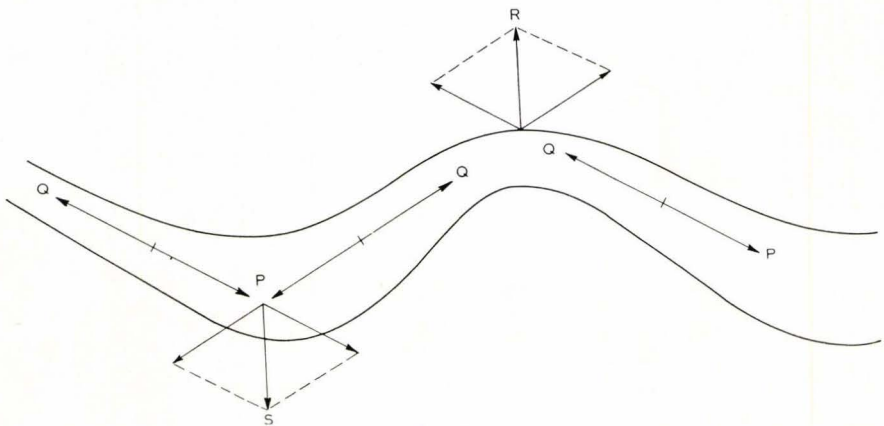

FIG. 7

In a swollen paint layer, the direction of the main stress is parallel to the surface of the layer. On the tops of elevations these stresses result in a force tending to lift the paint film. In the depressions the resultant force is, by contrast, directed towards the substrate

The characteristic picture of a blistered surface is quite different from that of a wrinkled surface. Wrinkling also is an effect of swelling but in this case the

dried film at the surface is swollen by the absorption of low molecular components from the liquid vehicle, between the dried surface layer and the substrate. However, there is no question of loss of adhesion, and consequently there is no process of detachment. From the beginning there is a liquid layer between the surface of the substrate and the dried film. Whereas the shape of wrinkles is random, the circular form of blisters testifies to a progressing detachment as the origin of blisters.

MEANS TO PREVENT BLISTERING

One way of preventing blistering would evidently be to prevent the paint film coming into contact with water. This, of course, is not a serious suggestion. Another possibility is to use media having much lower coefficients of swelling than those based on resins modified with drying oils, but there are well-known reasons why this solution of the problem is not acceptable. However, it is known that blisters can only be expected in those places where liquid water remains for long periods of time. Therefore, much damage can be prevented by using only, for such places, other and perhaps more expensive media.

It can be seen that it is not water itself that is the culprit, but the alkalinity of the water. Alkyd resins and many other media cannot resist water with a pH above 7. It is, therefore, of the greatest importance to pay great attention to the pigments used and to avoid pigments which have too alkaline character, or pigments with an additive which increases the alkalinity of water.

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