# The Linear Visco-Elastic Behaviour of Paint Films as a Function of Time and Temperature*

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*Summary*

Two varnishes, one composed of pure bodied linseed oil and the other of the same oil cooked with rosin, have been investigated extensively according to the method of mechanical spectroscopy, which is essentially an analysis of the time-dependent elastic behaviour of a material. The shape and the temperature-dependence of the approximate retardation spectra are calculated from creep-rate measurements on the one hand and from damping experiments on the other. It is shown that these two different experimental approaches are equivalent, as can be predicted from theory. The spectrum of retardation times is determined by the molecular rate processes and gives the relation between the sizes and the relative frequency of the molecular aggregates participating in the Brownian movement. From the measurements it can be concluded that the cooking of the oil with rosin results in the building up of much bigger aggregates.

If the elastic spectrum of the paint material and the changes effected by irradiation and leaching by water are known, it is possible to make a prediction about the performance in practice. This hypothesis has been tested on two varnishes and on four selected paints and has been fully confirmed. It may be specially noted that the effect of rosin in decreasing considerably the resistance to weathering can be ascribed entirely to the water-sensitivity it induces.

## INTRODUCTION

The investigations described here resulted from an attempt to solve the problem of the rational and scientific testing of organic coatings. There must exist an intimate relationship between the mechanical properties of the paint layer and the performance of the paint in practice. One of the most serious defects of a paint consequent on outdoor exposure is cracking of the film. Now the formation of a crack logically involves the existence of stresses and shear forces in the layer, which could grow up to the limit, *i.e.*, the ultimate tensile strength. The causes of these dangerous forces are the deformations to which the paint layer is subjected as an effect of thermal expansion and swelling by variations of the temperature and the relative humidity of the atmosphere. These deformations are completely determined by the supporting material and the paint layer is forced to follow its expansions and contractions. Not only cracking but gloss-retention also is mainly a matter of mechanical properties. The collision of dust particles with the surface of the layer can cause very high local stresses which result in the ,formation of micro-cracks. While deformations of the first kind are very slow gloss-retention is mainly the effect of resistance to very rapid deformations. The formation of cracks therefore is entirely dependent on the magnitude and rate of the stresses to which the paint layer is subjected. So long as the modulus of elasticity of the paint has a low value no formation of cracks will occur.

The mechanical properties of a visco-elastic material, such as paint, are functions of the rate of deformation and of the temperature. The parameters can be varied by changes in the chemical composition of the material. The main causes of these changes are of three sorts. In the first place we have the ageing of the paint, which is nothing else but the drying process continued, a reaction decaying exponentially with time. The second and the third causes are

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the actions of water and radiation, to which the paint is exposed during weathering. These also are reactions decaying with time, being, however, highly dependent on the intensity of the radiation and the quantity of water in contact with the paint. In any case it is certainly not necessary to wait years while the paint weathers in order to estimate the influence of these factors. An exact measurement of the mechanical properties and the changes of these properties with time and as a result of the influence of radiation and moisture makes it possible to predict the effect of weathering over a long period.

## THEORETICAL

In regard to the mechanical properties we have to distinguish between the linear region, where the deformations are so small that proportionality exists between stress and strain, the non-linear region, and the ultimate properties-tensile strength and elongation at break. For paints composed of oils and oil-modified resins the linear region extends up to 20 per cent elongation and more. It is only for the linear behaviour that a relatively simple theoretical treatment of the phenomena is possible.

The mechanical behaviour for small values of the deformation can be determined by various experimental procedures. For the shorter time-ranges dynamic experiments, such as damping measurements, are most suited and for slow deformations we can use stress relaxation and creep measurements. As discussed in the foregoing section, both the slow and the rapid deformations are important for a more fundamental understanding of the behaviour of the paint in practice and so we need the whole range of these experimental techniques for a complete and satisfactory description of the mechanical properties.

The data directly obtained from these various experiments are not very suited to an interpretation of the phenomena in terms of molecular rate processes, nor to a purely phenomenological description by means of models composed of springs and dashpots. From a theoretical point of view it is much more desirable to describe the material by means of the so-called spectra of relaxation or retardation times.

Making use of the concept of models, the time-dependent elastic behaviour of a high polymer in an experiment with constant strain can be represented by an infinite series of Maxwell elements coupled in parallel. In the case of constant stress the most adequate model is an infinite arrangement of Kelvin elements coupled in series. The integrated Maxwell model can be described mathematically by a relaxation spectrum, that is, the function connecting the moduli and the relaxation times of the individual elements. The retardation spectrum is a function of the reciprocal moduli (the compliances) and retardation times of the integrated Kelvin model.

There exists an extensive literature on the relations between the spectra and the experimental data. An exact calculation of the spectrum from the creep function requires a Laplace transformation, which is only possible if this function is given in an analytical form. This is hardly ever the case. Creep and stress relaxation are only available as graphs. The most general discussion of the derivation of the spectra from the empirical functions has been given by Schwarzl[1]. This author pointed out that a series of approximations of increasing accuracy exists in which the first member contains the first time derivative of the creep or

the stress relaxation. Higher approximations involve also higher time derivatives. To obtain an approximation of a higher resolving power, it is therefore necessary to have available the rate of creep, or, still better, of acceleration of the creep. The determination of these higher approximations is generally considered as a matter of increasing experimental difficulty. However, this is to a certain degree a prejudice, which is decidedly not true for the first derivative, the rate of creep. In a creep experiment the elongation of the sample is determined over long time intervals, extending from a few seconds to many hours after the moment of loading. During this time all perturbations which are inevitable, such as temperature fluctuations and insufficient stiffness of the support, accumulate, resulting in a great inaccuracy of the measurements for the longer times. For a velocity measurement, however, only a microscopic increase of elongation over a very short time interval has to be determined at successive moments. This is easier as the demands on the instrumental equipment are less severe.

For the shorter time ranges we are committed to dynamic experiments, either free or forced vibrations. However, when the sample has the shape of a thin and slack film, transverse free vibrations can tell us nothing about the elastic constants, because in this case the frequency of the oscillation is almost wholly determined by the tension and only to a negligibly small extent by the elastic modulus. Moreover, transverse vibrations are undesirable because of their large damping by the air. So longitudinal or torsional forced vibrations are most suited for these materials. Longitudinal vibrations have the advantage of a geometrically simple deformation.

Decreasing the temperature will result in a shift of the spectrum to the longer time ranges, whereas increase of temperature gives a shift to shorter times. We can understand these facts both with the help of the phenomenological model with springs and dashpots, and also by considering the influence of the temperature on the Brownian movement of the various segments of the high-polymeric chain molecules. A change in temperature will result in an increase or a decrease of the viscosity of the liquids in the dashpots, which gives corresponding changes in the retardation and relaxation times. Generally we cannot hope that the shift will not involve a change in the shape of the spectrum. Schwarzl and Staverman[2] have called those materials which show a temperature shift in their spectrum without change in shape, thermo-rheologically simple materials. For these materials it is possible to determine the whole spectrum over a very extensive time scale using measurements carried out within a much more limited time range but at various temperatures.

For determination of the spectrum in the longer time range we have for the experimental methods the choice between creep measurements and stress relaxation. However, only the first can give us an unambiguous picture of the linear elastic behaviour when the material shows retarded elasticity besides viscous flow. In principle this possibility always exists and so a creep experiment is most suited for an exact description of the mechanical behaviour in the longer time ranges.

As mentioned in the foregoing section, the first approximation of the retardation spectrum is not the creep itself but the logarithmic time derivative of the creep function. We have, $\gamma$ being the strain, $S$ the tension and $t$ the time:

$$\frac{d(\gamma/S)}{d\log t} = 2.3 \frac{d(\gamma/S)}{dt} \quad t \sim L(\log \tau) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $L(\log \tau)$ is the continuous spectrum of retardation times. The resolving power of this first approximation is about one decade; that means, when the real spectrum contains two maxima with a mutual distance less then one decade in the logarithmic time scale, the first approximation is not capable of separating these maxima. The resolving power is actually somewhat lower, as we must take into account the experimental inaccuracy of the measurement itself.

For the shorter time range damping measurements are most suited. It is necessary to make use of an auxiliary elasticity, since the thin and slack paint films do not have sufficient stiffness to produce high frequencies. A simple arrangement, which was used for the measurements, as stated below, is shown in Fig. 1. On a swinging beam, attached to a steel spring, two film strips were clamped. The other ends of the strips were attached to a fixed point. During each oscillation of the beam one film was stretched and the other could contract. It was necessary to maintain a static tension in the films during the measurement in order to ensure that the strips were always stretched. The damping of the beam was measured first with the films stretched and a second time without the films. From the two damping constants the energy dissipated in the films could easily be calculated. Using steel springs of various lengths and thicknesses and by loading the beam with various weights, it is possible to vary the frequency of the oscillation. In this experiment the deformation is constant and we determine in fact the imaginary part of the complex elastic modulus, $E'$. This quantity is a first approxi-

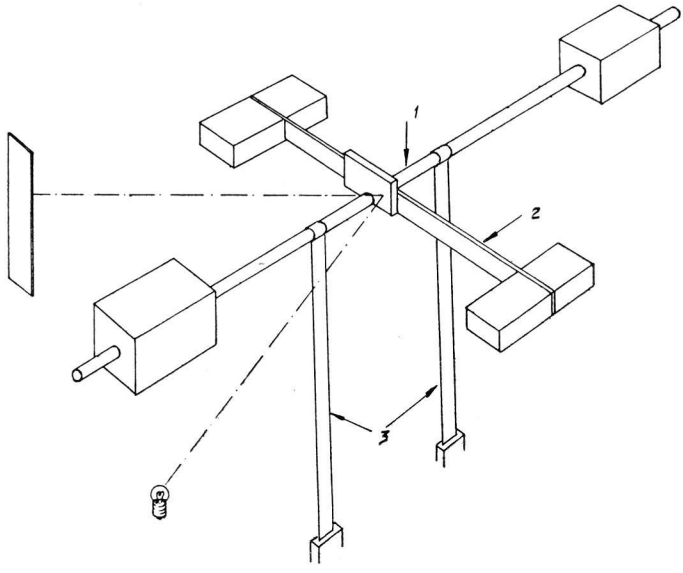


FIG. 1. APPARATUS FOR MEASURING DAMPING IN FILM STRIPS
1, Swinging beam. 2, Steel spring. 3, Film strips.

mation of the spectrum of relaxation times. If we represent this spectrum by $M(\log\tau)$ it follows that[1]:

$$\frac{2E'}{\pi} \sim M(\log \tau) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The resolving power of this approximation is somewhat lower than that of the creep rate.

From creep-rate measurements, where the tension is constant, we obtain an approximation of retardation times, and by damping experiments, where the deformation is constant, we get an approximation of the relaxation spectrum. Both spectra give an unambiguous description of the mechanical behaviour of the material, though they are not identical. For a comparison of the two experiments it is necessary to transform one function into the other. A transformation formula has been given by Gross[3].

## Experimental Technique

For the preparation of the paint and varnish films a certain quantity of the material, depending on the desired thickness of the layer, was poured out on a glass disc covered with tinfoil. By centrifuging the disc it was possible to spread out the paint so that a layer of uniform thickness was obtained. After drying, the tinfoil together with the paint was cut in strips of about 16 cm. length and a width of 0.75 cm. The metallic layer was then dissolved with mercury.

For the measurement of the creep rate, films were attached to a very stable support, free from vibrations, and enclosed in a thermostatically controlled box. The temperature of this box could be varied between $-5°C$ and $+50°C$ (Fig. 2). At the lower end of the film was attached a little hook carrying the load

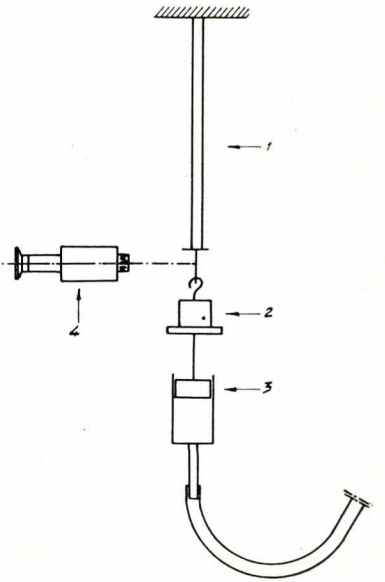


Fig. 2. Principle of Creep-Rate Measurement

1. Film strip
2. Load
3. Table, movable by mercury pressure and carrying the load
4. Microscope

by means of a silk thread. The load itself could be raised and lowered with a little platform movable by mercury pressure. The creep of the lowest end of the film strip could be observed with a microscope with high magnification (8mm. objective) and provided with an eyepiece micrometer. The time necessary for the film to creep over a fixed number of lines of the micrometer was measured with a stopwatch. This time, $\delta t$, was directly plotted on a double logarithmic scale against the running time, *i.e.*, the time elapsed since the moment of loading. The weight of the load was chosen in such a way that a reasonable rate of creep was obtained; in most cases it was necessary to use weights varying between 3 and 40 grams, corresponding to a tension between 0.08 and $1 \times 10^7$ dyne/cm.$^2$. The first measurement of the creep rate was possible about five seconds after the moment of loading, the last measurement was to a very high degree determined by the character of the creep function, but generally it was possible to follow the creep-rate function over a time interval of 36 hours. Thus the time interval covered by this experiment lay between 10 and $10^5$ seconds.

From the plot of $\delta t$ against the running time the first approximation of the retardation-time spectrum was obtained by means of a simple graphical construction. We have:

$$\log L(\log \tau) \sim \log \frac{\mathrm{d}\,(\gamma/S)}{\mathrm{d}\,\log t} = \log 2.3 \frac{\mathrm{d}\,(\gamma/S)}{\mathrm{d}t}\, t = \log t - (\log \delta t - \log f)$$

where $f = 2.3\ \delta(\gamma/S)/\delta\gamma$, and, being determined from the number of lines of the eyepiece micrometer connected with the measured time $\delta t$, has the dimensions cm.$^2$/dyne.

Fig. 3 gives a picture of a complete set of measurements made in this way

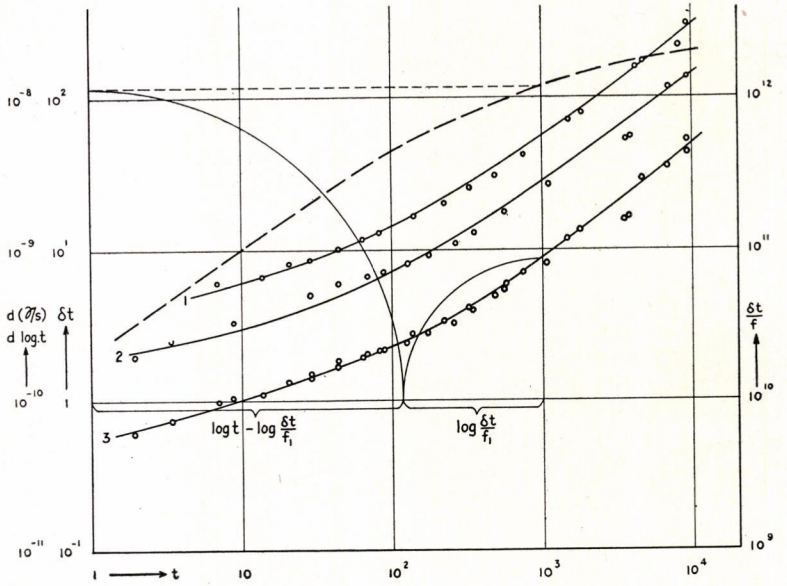


FIG. 3. RESULT OF A SERIES OF CREEP RATE MEASUREMENTS

with an alkyd resin varnish. The experiment was executed with two different film strips of the same material, having the same dimensions but bearing different loads. The points of curve 1 relate to measurements of the strip with the lowest load, that of curve 2 to the strip with the highest load. The value of the factor $f$ was for all measurements of the first strip the same, namely $6{\cdot}0\times10^{-10}$ cm.$^2$/dyne and for all measurements of the second strip: $3{\cdot}3\times10^{-10}$ cm.$^2$/dyne. Now, if the mechanical behaviour of this varnish is linear, then the superposition principle of Boltzman is satisfied and consequently all values of the measured times, $\delta t$, from both film strips must fall on the same curve when we divide these values by the corresponding tensions, $S$. In a logarithmic time scale this means a shift of both curves over a part of a decade, namely the part indicated by the factor, $f$, and, at the same time, multiplication of the numbers indicating the decades of the ordinate axis by $10^{-10}$. In Fig. 3 these shifts have been made and the result is that indeed all points lie reasonably well on one and the same curve (curve 3).

All paints and varnishes so far investigated exhibit this linear behaviour up to elongations of 20 per cent and more.

The dotted curve in Fig. 3 is the logarithmic time derivative of the creep rate obtained from the experimental curve 3 by means of a construction, indicated in the figure for one point of the curve, marked by a cross.

For the shorter time range, damping measurements were made. The instrument used for these experiments is described in the foregoing section. The energy dissipated during one cycle in the film strips is [4]:

$$A=\pi E'\gamma^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The reasons why the movement of the swinging beam is damped are as follows: in the first place energy is dissipated in the steel spring, secondly, there is an energy dissipation in the strips and, finally, we have a small air damping. A simple calculation shows that:

$$E'=\frac{Cl}{\pi a^2 D}\left[\left\{\exp\frac{2}{\omega}(k_2-k_1)\right\}-1\right] \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $E'$ is the imaginary part of the elastic modulus of the samples, $k_2$ and $k_1$ are the logarithmic decrements of the oscillation of the beam, first when the film strips are stretched and afterwards when the films are removed, $C$ is the spring constant of the steel spring, $l$ and $D$ length and cross section of the films, $a$ the distance apart of the ends of the strips which are clamped to the beam, and $\omega$ the frequency of the oscillation. With this instrument it was possible to vary the frequency from 0.2 sec.$^{-1}$ to 30 sec.$^{-1}$. This experiment thus embraces a time range of about two decades.

The quantity $2E'/\pi$ is a first approximation of the spectrum of relaxation times. The accuracy of these dynamic measurements was, however, less satisfactory than attained with the static creep experiments.

In Fig. 4 the value of $2E'/\pi$ is plotted against the logarithm of the reciprocal of the frequency for a varnish made from linseed stand oil cooked with 15 per cent of rosin. In order to compare these measurements with the results of creep

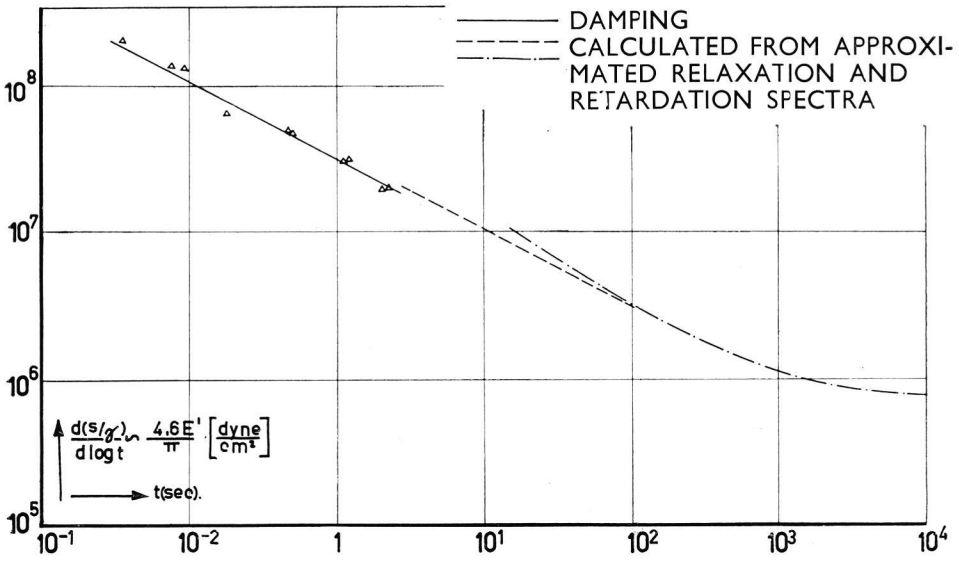


FIG. 4. COMPARISON BETWEEN DAMPING MEASUREMENTS AND CREEPRATE MEASUREMENTS

rate determinations, the same figure shows the relaxation spectrum calculated from the first approximation of the retardation spectrum by means of the transformation formula of Gross[4]:

$$M \log \tau = \frac{L \log \tau}{\left[\int_{-\infty}^{+\infty} \left(\frac{\tau}{\tau - u}\right) L \log u \, d \log u\right]^2 + \left[\frac{\pi}{2{\cdot}3} L \log \tau\right]^2} \quad . \quad . \quad . \quad (5)$$

where $u$ is an integration variable. From this relation it follows that the whole retardation spectrum must be known in order to carry out the transformation, which generally will not be the case. Our measurements covered a time range extending from 2 to $10^4$ seconds; it luckily so happened that the value of the function $L\log\tau$ was very small for times below 10 seconds and that the factor $\tau/(\tau-u)$ was small for high values of $u$. So the contributions to the integral in the denominator of equation (5), arising from the time ranges not covered by measurements, were negligible. As can be seen from Fig. 5, the correlation between the two series of measurements is reasonably good. We may conclude from these results, that dynamic and static measurements are substantially equivalent, and that the linear behaviour of these materials is in full accordance with the predictions of the theory.

## RESULTS

Fig. 5 shows a set of measurements made with pure linseed stand oil after a drying time of 30 days. The full curves in this figure are the logarithmic time derivatives of the creep rate obtained from measurements at various tempera-

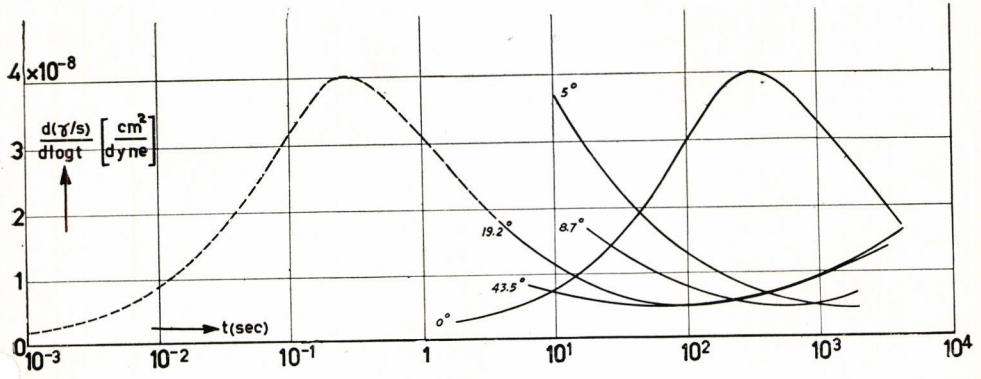


FIG. 5. APPROXIMATED RETARDATION SPECTRUM OF A LINSEED STAND OIL VARNISH AT ROOM TEMPERATURE

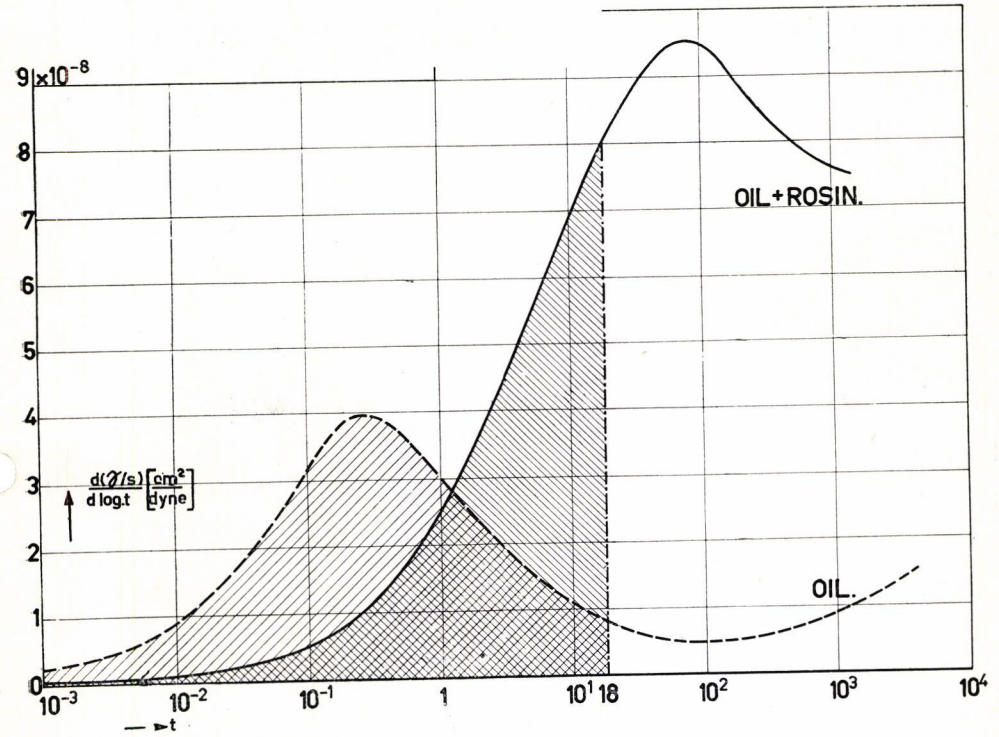


FIG. 6. APPROXIMATED RETARDATION SPECTRUM OF A VARNISH COMPOSED OF LINSEED STAND OIL COOKED WITH ROSIN

tures. The ordinate axis is not logarithmically but linearly divided. It was possible to shift the spectra corresponding to 0°, 5° and 8.7°C to the left parallel to the time axis without changing their shape, in such a way that a continuous line could be obtained, giving the spectrum over a time interval of seven decades. This is the dotted curve in the figure. That means that this varnish shows an ideal time-temperature shift, and belongs to the class of the thermo-rheologically simple bodies. The spectrum has a maximum at 0.2 sec. and a second maximum probably at about $10^5$ sec. which lies outside the region which was experimentally accessible.

Fig. 6 gives the first approximation of the retardation time spectrum of linseed stand oil cooked with rosin after 15 days' drying time. This varnish showed some viscous flow (irreversible recovery), but the effect had disappeared after 30 days. The spectrum is indicated by the full curve in this figure, which was obtained in the same way as the spectrum in Fig. 5 from measurements made at various temperatures, by shifting the lines in such a way that a continuous curve was built up. This varnish also was a thermo-rheologically simple substance. For a comparison with the varnish from pure linseed stand oil, the spectrum from Fig. 6 has been drawn again in Fig. 7 as a dotted curve. There is a striking difference between the two spectra. The effect of the rosin is to cause a shift in the maximum from 0.2 sec. to about 80 sec., while the height of the maximum has also considerably increased. These first approximations are the logarithmic time derivatives of the creep and so the area between the curve, the logarithmic time axis and the ordinate at epoch $t$, is a direct measure of the total elongation of the film strip at that moment. Now, if we trace an ordinate at the point, $t=18$

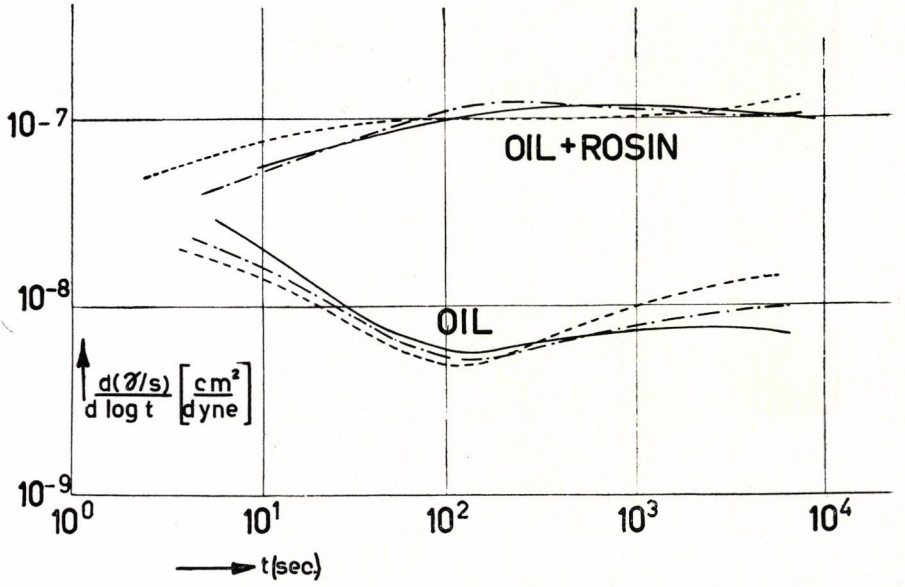


FIG. 7. INFLUENCE OF IRRADIATION

seconds, it appears that the areas under both curves are equal and correspond to an elongation of 8 per cent at a tension of 1 kg./cm.$^2$. This means that when the film strips are stretched at a deformation rate smaller than 8 per cent in 18 seconds it is the rosin-containing varnish which gives the impression of being the softer material, whereas, if the rate of deformation exceeds this limit, it is the pure oil which is the softer.

The position of the maximum on the time axis is dependent on the size of the molecular aggregates which participate in the Brownian movement, whilst the height of the maximum is a measure of the relative frequency of these aggregates. The effect of the cooking with rosin is, therefore, a large increase in the bigger aggregates and a decrease in the smaller ones, and it is obviously not a simple mixing but a building-up of new chemical links. The width of the maximum is also changed. This width is determined by the dispersion of the molecular weights of the aggregates, which dispersion is strongly increased by the cooking with rosin. The half-width value of the first maximum of the pure oil is about two decades, but for the colophony-containing material more than four decades. Therefore, it seems very probable that, not only are smaller molecules from the pure oil varnish built up into larger ones, but also that the very large molecules (causing the second maximum) are broken down into smaller ones.

It will be clear that the method of "mechanical spectroscopy" can give information on the molecular composition of the material.

## Mechanical Behaviour and Performance in Practice

As stated before, we must expect that the mechanical properties of the paint material will change during the life of the paint. Therefore, we have to consider the following questions:

What is the relation between the age of the paint and its mechanical properties?
What is the influence of radiation?
What is the influence of leaching of the paint layer by water?

In regard to the first of these problems we know that, in general, ageing is a process going on very slowly when the paint layer is kept at constant temperature and humidity. Ageing is nothing else than the continuation of the drying process itself, which decays exponentially with time. For the above-mentioned varnishes creep-rate measurements were made 35 days and 70 days after application. The difference between the curves obtained was very small.

Fig. 7 shows the influence of ultra-violet radiation. In this and in all following figures the ordinate axis is logarithmically scaled; in the interpretation of the figures it is very important to keep this in mind. The lowest three curves in Fig. 7 relate to the pure oil varnish, the higher curves to the oil-rosin varnish. The dotted curves are the approximated spectra of the untreated varnishes and therefore the same as those shown in Figures 5 and 6 (vertical axis has logarithmic scale). The interrupted curves are the spectra of the films after an irradiation of 18 hours with a very powerful ultra-violet light source (1,000-watt high-pressure mercury arc). The full curves are the spectra of the films after an irradiation of 37 hours. All measurements were made at room temperature, which means that only the spectrum in the time interval from 5 to 10,000 seconds could be investigated.

The effect of the irradiation is relatively small. This is in agreement with expectations from consideration of the light absorption of a thin colourless varnish film, which is small even in the region of the shorter wavelengths; and without absorption nothing can happen. However, these relatively small effects are very characteristic. With the pure oil varnish there is an increase of the compliances in the shorter time range and a decrease in the region of the longer times. The rosin-containing varnish on the contrary shows a decrease of the compliance in the shorter time region, whilst there is a distinct shift of the maximum to the right of the spectrum. From the viewpoint of practice, the pure oil varnish has attained a somewhat better resistance against the dangerous forced deformations to which the varnish layer is exposed but the rosin-containing varnish is in a less favourable condition.

Fig. 8 gives a picture of the influence of water on the varnish. The dotted curves in this figure again are the approximated spectra of the untreated varnishes, the full curves are the spectra of the films after 24 hours of leaching by water. Both the spectra are radically changed. The rosin-containing varnish has lost compliance to a considerable degree (logarithmically scaled ordinates) in the shorter time range and gained compliance in the region of the very long times, whereby the maximum is shifted to the right of the spectrum. The pure oil varnish has gained compliance in the region of 100 seconds and the slope of the line gives an indication that the first maximum is now somewhat lower.

What conclusions can we draw from the results of this mechanical spectroscopy? The first fact is that we find formation of bigger molecular aggregates

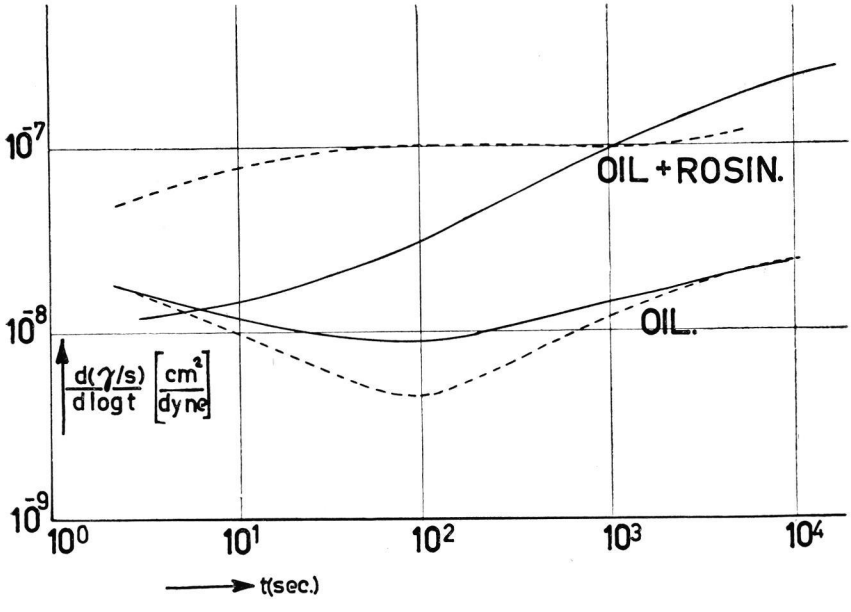


FIG. 8. INFLUENCE OF LEACHING BY WATER

on cooking with rosin. The second fact is that these aggregates have a greatly increased water-sensitivity. The effect of water on the colophony-containing varnish is to cause a further increase in the dimensions of the molecular aggregates, and consequently an immobilisation of the Brownian movement. The water-sensitivity of colophony is not a matter of extraction of soluble components, but on the contrary a reaction of the varnish with water, in such a way that new chemical links are formed.

What about the possibility of predicting performance in practice? As has been explained, there are two sorts of forced deformation to which the paint layer is subjected during outdoor exposure: very rapid deformations caused by collision with sand and dust, which are responsible for the loss of gloss, and the slow ones, which are the result of thermal expansions and contractions. For resistance against rapid deformations it is necessary for the material to have a high compliance in the region of the short times. Therefore we can expect that the pure oil varnish will have a high gloss retention and that the rosin-containing varnish will soon lose its gloss. This prediction was found to be in perfect agreement with the results of outdoor exposure. Table I gives the gloss measurements for both the varnishes.

TABLE I

GLOSS RETENTION

| Number of months outdoor exposure .. | 0 | 1 | 6 | 10 | 15 |
|---|---|---|---|---|---|
| Percentage of gloss for the pure oil varnish (Ideal mirror=100) .. .. .. | 5.2 | 4.5 | 3.5 | 3.5 | 2.4 |
| Percentage of gloss for the rosin varnish .. | 4.9 | 3.7 | 3.0 | 2.0 | 0.8 |

It is beyond doubt that the resistance against cracking of the pure oil varnish must be greater than that of the rosin-containing varnish. After ten months' outdoor exposure the latter showed a few cracks and after 15 months the cracking was heavy. The pure oil varnish remained intact. It is the increased water-sensitivity of the colophony product which is responsible for this state of affairs. If kept indoors the test panels remain intact.

TABLE II

COMPOSITION OF FOUR PAINTS IN ORDER OF DECREASING DURABILITY

| Paint number | Vehicle composition | Pigment | Pigment content % |
|---|---|---|---|
| 1 | Alkyd resin (31 per cent phthalic anhydride) | Red iron oxide | 42.5 |
| 2 | Alkyd resin (31 per cent phthalic anhydride) | Lead titanate | 62.5 |
| 3 | Linseed stand oil .. .. .. .. | Zinc oxide | 57.5 |
| 4 | 4 : 1 Linseed stand oil—phenolic resin varnish | Zinc oxide | 32.5 |

## MECHANICAL SPECTROSCOPY AS A PRACTICAL METHOD OF EVALUATION

In order to test the hypothesis stated above, a more extensive investigation was set up. Four paints were prepared, of which the order of resistance against weathering was established unambiguously by means of outdoor exposure tests with a great number of test panels. The composition of these paints is shown in Table II.

Table III gives the result of the outdoor exposure, the scoring being as follows:

0=intact,
1=very slight cracking,
2=moderate cracking,
3=bad cracking.

TABLE III

DEGREE OF CRACKING OF THE PAINT LAYER AFTER AN EXPOSURE TIME OF $n$ YEARS

| Paint | $n$=0.5 | 1 | 1.5 | 2 | 2.5 | 3 | 3.5 | 4 | 5 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 1 | 1 |
| 2 | 0 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 3 | 0 | 1 | 1 | 2 | 3 | | | | |
| 4 | 3 | | | | | | | | |

The approximated retardation spectra of these four paints at room temperature were determined, as well as the changes in these spectra through ageing, the influence of ultra-violet radiation and the effect of leaching by water.

Fig. 9 gives the spectra of the four paints after a drying time of 35 days (dotted curves) and after a drying time of 105 days (full curves). The arrows in the figure indicate the direction of the changes effected by ageing. In the region critical for cracking, paint 1 has the highest value of the compliance, then follows 3, then 2, and, as the paint with the lowest value of the compliance, 4. Seventy days later we find a remarkable effect. With paints 3 and 4 the ageing consists in a decrease of the compliance, greater with 4 than with 3. The spectrum of 1 is about the same as that after 35 days drying time, whilst with 2 the compliance in the critical region is increased. So after 105 days' drying time the sequence of decreasing compliance is: 1, 2, 3, 4.

Fig. 10 gives a picture of the influence of ultra-violet radiation. After an irradiation of 5 hours with a high pressure mercury arc the compliances of the paints 1 and 2 are increased and that of paints 3 and 4 are decreased. The dotted curves in this figure are the spectra of the untreated varnishes after a drying time of 105 days and the full curves are the spectra after irradiation. The effect of ultra-violet light on these paints is considerably greater than on the two varnishes mentioned above. We can understand this behaviour in considering the absorption, which is considerably greater with a pigmented material than with a varnish. It is remarkable that an alkyd resin vehicle at the beginning is growing softer through irradiation. The ageing for this material consists thus in an increase

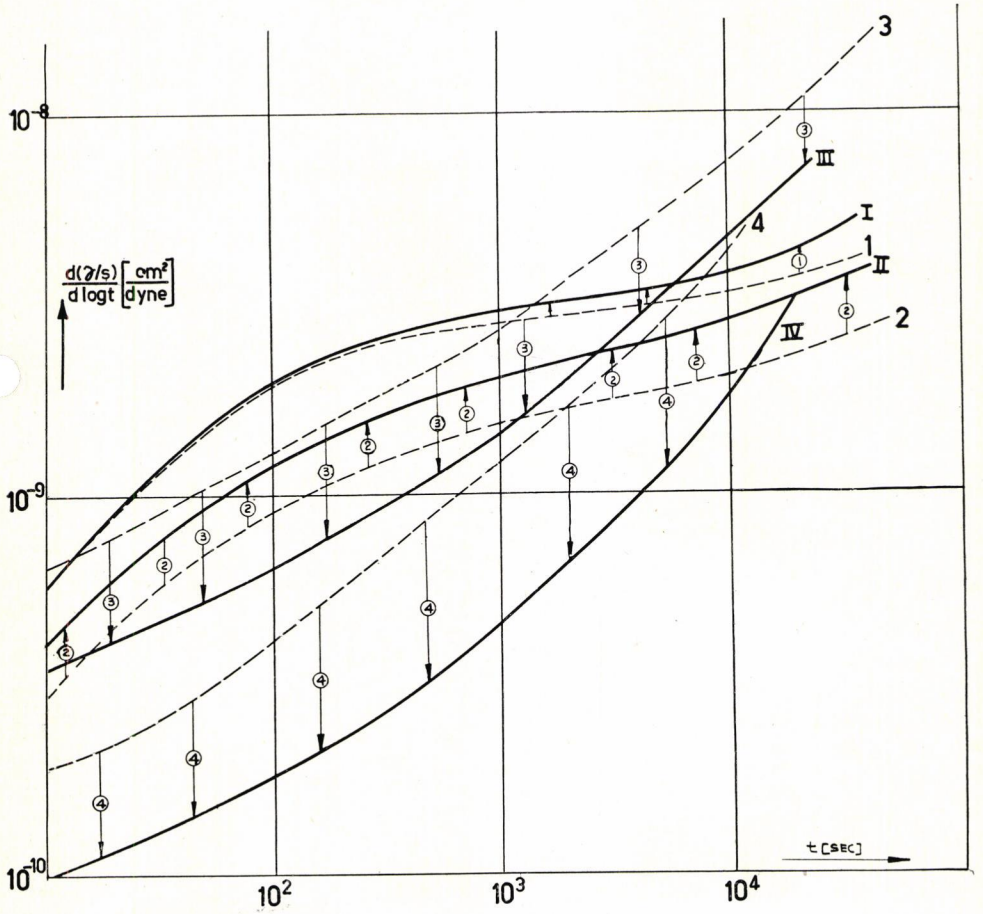


FIG. 9. APPROXIMATED RETARDATION SPECTRA OF FOUR PAINTS: CHANGES ON AGEING

of the compliance and, therefore, it seems very probable that the ageing is to a very high degree an effect of irradiation.

Fig. 11 shows the effect of irradiation for 10 hours of the paints 1 and 2. Again the dotted curves are the spectra of the untreated paints after a drying time of 105 days and the full curves are the spectra after 10 hours irradiation. The initial increase of the compliance is now changed to a decrease. The slope of the left of the curves gives an indication that a new maximum in the range of the short times has been built up. The spectrum is "linseed-oil-like". Considering the effects of irradiation we can say that the sequence of increasing deterioration caused by irradiation for these four paints is: 1, 2, 3, 4.

Fig. 12 gives the results of experiments with leaching by water for 24 hours. Again the dotted curves are the approximated spectra of the untreated paints

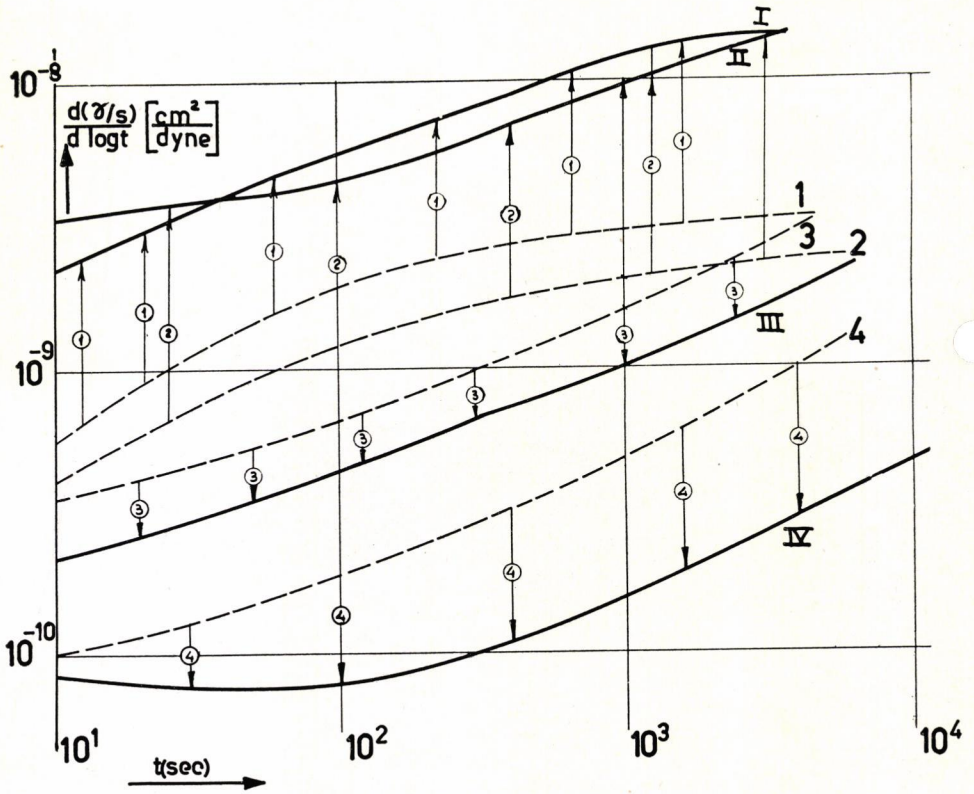


FIG. 10. INFLUENCE OF IRRADIATION

after a drying time of 105 days. The full curves show the same spectra after leaching with water for 24 hours. The arrows give the direction of the changes in the curves. With all the spectra the compliances over the whole range of retardation times are diminished. After the experiment the sequence of decreasing compliance is still: 1, 2, 3, 4.

For a complete investigation it is necessary to know both the linear behaviour of the material and the ultimate properties. To make a prediction about resistance to forced deformations we need information about the tensile strength and the elongation at break. The determination of these quantities was carried out using an electronically recording dynamometer. The speed of the clamps of this instrument could be varied. The minimum value was 10 per cent elongation per minute, the highest 1,000 per cent per minute. Table IV gives the values thus obtained.

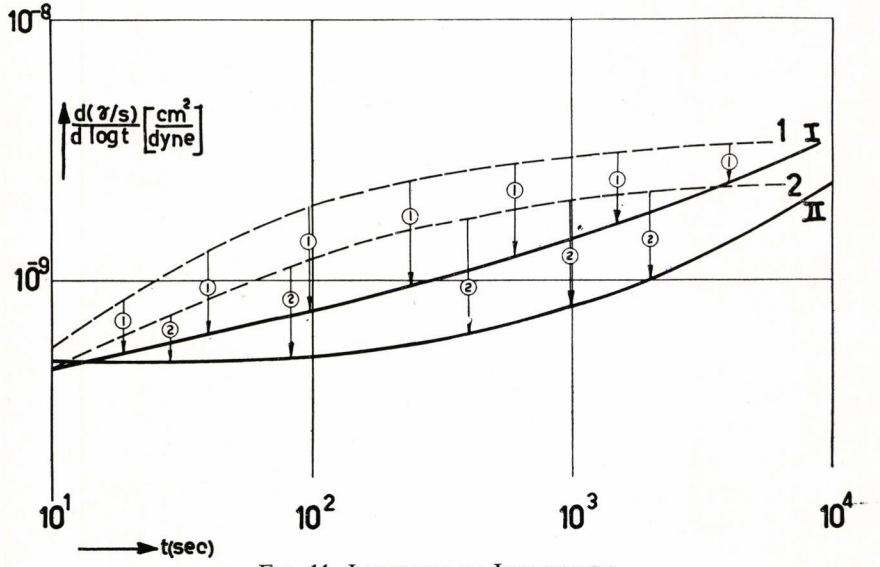


FIG. 11. INFLUENCE OF IRRADIATION

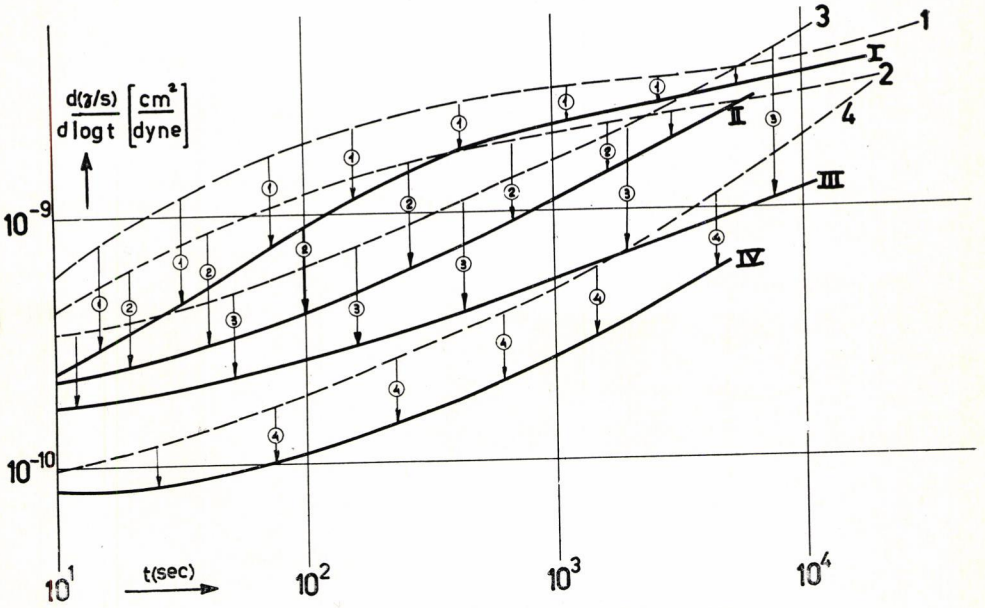


Fig. 12. INFLUENCE OF LEACHING BY WATER

TABLE IV

TENSILE STRENGTH AND ELONGATION AT BREAK OF FOUR PAINTS WITH DIFFERENT DURABILITIES

Rate of elongation 10 per cent per min.

| | | Paint number 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Tensile strength (kg./cm.²) | untreated | 93 | 80 | 60 | 97 |
| | 24 hr. leaching | 100 | 81 | 60 | 76 |
| | 5 hr. irradiation | 80 | 69 | 72 | 120 |
| Elongation at break (per cent) | untreated | 85 | 70 | 34 | 36 |
| | 24 hr. leaching | 83 | 71 | 26 | 9 |
| | 5 hr. irradiation | 88 | 70 | 30 | 5 |

Rate of elongation, 100 per cent per min.

| | | | | | |
|---|---|---|---|---|---|
| Tensile strength (kg./cm.²) | untreated | 112 | 103 | 79 | 109 |
| | 24 hr. leaching | 136 | 111 | 90 | 145 |
| | 5 hr. irradiation | 134 | 110 | 63 | 154 |
| Elongation at break (per cent) | untreated | 62 | 54 | 22 | 19 |
| | 24 hr. leaching | 78 | 51 | 23 | 9 |
| | 5 hr. irradiation | 75 | 63 | 21 | 4 |

Rate of elongation 1000 per cent per min.

| | | | | | |
|---|---|---|---|---|---|
| Tensile strength (kg./cm.²) | untreated | 160 | 137 | 122 | 192 |
| | 24 hr. leaching | 145 | 141 | — | — |
| | 5 hr. irradiation | 152 | 124 | — | — |
| Elongation at break (per cent) | untreated | 69 | 41 | 20 | 20 |
| | 24 hr. leaching | 65 | 39 | — | — |
| | 5 hr. irradiation | 71 | 57 | — | — |

In considering the figures in Table IV we must take account of the much lower accuracy which can be attained in determining ultimate properties than in measuring mechanical properties at smaller values of the tension, when no discontinuous rupture occurs. The uncertainty in the figures of Table IV is about 15 per cent of the absolute value. The first remarkable thing is that the tensile strength is nearly independent both of the composition of the paint and of the effects of irradiation and of water leaching. Of course the number of the paints is too small to establish a general rule, but it suggests that ultimate properties are less characteristic of the material than the behaviour at small deformations. In the figures representing the elongation at break, we find again

the order 1, 2, 3, 4. This follows from the great differences in compliance between the various paints; the elongation of the paint with lower compliance must be smaller in order to reach the tensile stress which has about the same value for all the paints. For the rest, the tensile strength of paints is always much higher than that of unpigmented vehicles; this phenomenon may be due to the fact that the pigment particles prevent the development and enlargement of the cracks. Summarising, we can conclude that the sequence of linear mechanical behaviour is in perfect agreement with the sequence of the performance in practice and that the hypotheses on which our experiments were based so far are affirmed.

## Conclusions

1. All paints and varnishes which have been investigated by the method of mechanical spectroscopy follow the superposition principle of Boltzman, their mechanical behaviour being linear up to elongation of at least 20 per cent. This means that the paint vehicle is amorphous and no crystallisation occurs when the material is stretched.

2. Alkyd resins and varnishes composed of linseed oil and stand oil do not show viscous flow. When cooked with rosin they show some viscous flow immediately after drying, but this disappears within three weeks.

3. The mechanical spectra of these varnishes and paints show a perfect time-temperature shift, which means that these materials belong to the class of thermo-rheologically simple substances. This behaviour greatly simplifies the process of determining the complete spectrum, as it is sufficient to measure part of a spectrum at various temperatures.

4. The first approximation of the retardation spectrum, derived from creep-rate measurements, is in agreement with the first approximation of the relaxation spectrum, derived from damping measurements. All these experiments are essentially equivalent and each can give a complete description of the mechanical properties within the region of linear behaviour.

5. For all the materials thus far investigated it has turned out that the ultimate properties, the tensile strength and the elongation at break, are less characteristic and to a much lower degree dependent on composition and pretreatment of the material, than the mechanical properties at small deformations.

6. The method of mechanical spectroscopy can give information on the size and the mobility of the molecular aggregates which participate in the Brownian movement. This information can be extremely useful in analysing the effect of oil-cooking and admixture with various resins.

7. When the mechanical properties of the paint film are investigated as completely as possible (linear behaviour and ultimate properties) and also the effects of ageing, irradiation and leaching by water, it is possible to make a prediction about the performance in practice with respect to the phenomena of cracking and gloss-retention.

## Acknowledgement

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## DISCUSSION

DR. A. JOBLING described some recent work carried out in Cambridge on the mode of rupture of thin films of a great variety of materials ranging from powders and pastes to solid polymers and vacuum-deposited metal films. The use of a deformable boundary (*e.g.*, rubber sheet) to impose any one of a wide range of rotational or irrotational shearing actions on the material results in the production of uniform break-up throughout the sample under test. Cracks appear in well-defined directions with a fairly clear periodicity. Fig. 13 illustrates a typical result (a paste of cornflour in decanol, stretched on a strip of rubber in a three-dimensional pure shear. An extension by a ratio, $\lambda$, along the x-axis is accompanied by contractions of $(\lambda)^{-\frac{1}{2}}$ in the $y$ and $z$ directions).

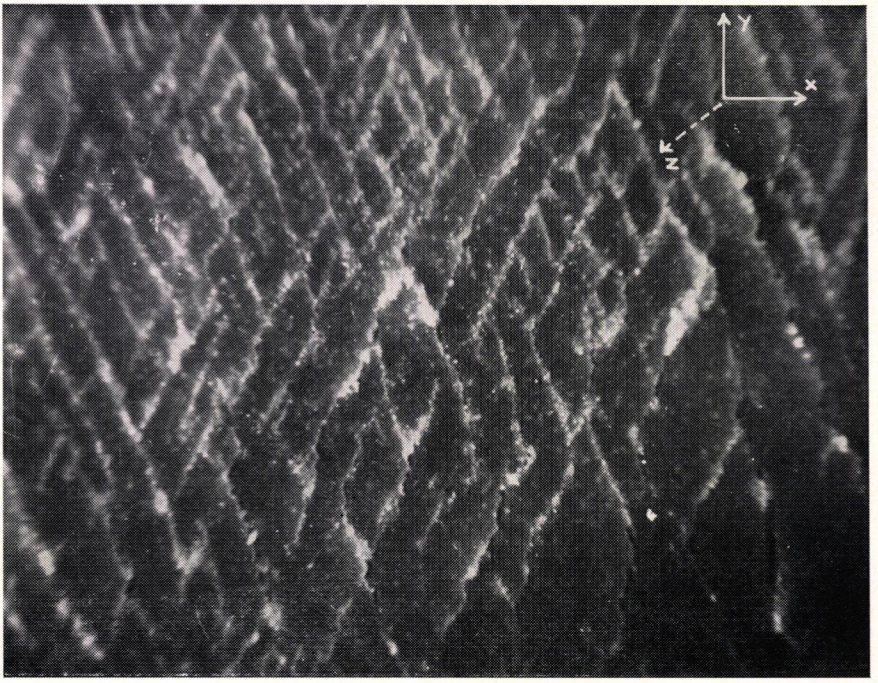


FIG. 13. RUPTURE OF A PASTE OF CORNFLOUR IN DECANOL

The most striking feature of the work is the similarity in behaviour of widely differing substances which has been observed. Since, in principle, it is possible to

measure all the stresses and strains involved in the deformation it is hoped that quantitative methods can now be developed for studying the transition from continuous flow to rupture.

A fuller account of this work is being prepared for publication.

*NOTE: In presenting his paper, Dr. Brunt had pointed out that it was unnecessary to postulate molecular attraction to account for viscosity. He considered the case of a perfect gas of very high molecular weight, whose molecules would thus have a very low thermal velocity. On compressing such a gas with a piston the equipartition of energy would take place at a finite speed, giving rise to a "dashpot" effect. The discussion that follows relates to this point.*

MR. R. B. WATERHOUSE confessed that he was a little puzzled by Dr. Brunt's picture of the cylinder of the ideal gas, because he could not see how the molecular weight of the gas would come into the matter at all. The energy of equal volumes of gases at the same temperature and pressure was a constant, whatever the molecular weight, and that meant that the momentum of the molecules was a constant. Therefore, although the molecules were moving slowly, they were, of course, much heavier. So that, when the large gas was compressed, the pressure exerted on the piston was surely just a function of the number of molecules encountered and their momentum. In both cases, if there were the same number of molecules and the average density were the same, and inasmuch as they all had the same momentum, he could not see why there should be any difference between gases of low and of high molecular weight.

DR. BRUNT said that, if the movement of the piston was infinitely slow, we should have at each moment an equilibrium distribution of the molecules, which meant that the molecular density should be the same at all points in the space and the pressure could be calculated by Boyle's law. But if the piston was moved at a finite velocity there would be an accumulation of molecules in the immediate neighbourhood of the piston and therefore the pressure on the piston would be higher than the equilibrium value. For an aeroplane flying with increasing velocity there would come a moment when the air changed from a soft body into a hard one. That is what we call passing the sound barrier. The critical velocity for the aeroplane to pass this barrier was the same as the mean molecular velocity of the air. A gas had a transition point in the same way as a high polymeric substance. For low velocities it behaved as a soft body, for high velocities it was a hard one. But the molecular weight of a gas was very small compared with a high polymer and therefore the mean molecular velocity was very high. So in most experiments with gases one did not observe the transition point.

DR. A. J. ELLEMAN said it had been pointed out that there was a possibility of correlation between the type of distribution obtained with retardation time and the molecular structure. He asked if Dr. Brunt had any information on the breadth of the retardation—time distribution and the molecular weight distribution of the non-volatile vehicle before oxidation.

With regard to the work reported on the effect of ultra-violet irradiation, he said there was no mention in the paper of the time that elapsed after irradiation before the measurements were made. In some work with which he had been concerned it had been found that even 100 hours after irradiation the film was still changing in its physical behaviour.

DR. BRUNT, replying to Dr. Elleman's second point, said he had waited 48 hours after irradiation. He confessed that he did not know that 100 hours after irradiation the equilibrium was not established. But he felt that there would not be a large effect because the times of irradiation were very short.

The investigations were very sensitive, and an irradiation of one or two hours

could be sufficient to give changes in the spectrum. So he thought that after two days the equilibrium was nearly established.

Regarding the first question, he said we must distinguish between molecular weight and the information we can obtain from retardation spectra. For a cross-linked material molecular weight in itself is a highly questionable concept. The spectra give an indication of the distribution of the masses taking part in the Brownian movement, but that is not the same thing as molecular weight, for we cannot distinguish between chemical and physical cross-linking.

DR. E. SUNDERLAND said the author had reported results where relaxation times and spectra had changed over periods of from 30 to 105 days in conditions of constant humidity and temperature; this work was important when we considered the methods used for accelerating the weathering of any paint. It seemed from the results given that we should achieve a better approximation to natural weathering if we waited longer than we did usually before applying the forces that we brought to bear on paint films during accelerated weathering. It appeared that our normal drying times of a few days were quite inadequate to establish the structure that a film would have if it were exposed only to the less brutal effects to which it was subjected during its normal life. It was up to the practical man to investigate the problem of the length of the conditioning period before applying the brutal forces of accelerated weathering.

DR. BRUNT commented that he could very well understand Dr. Sunderland's objections. It was said that the times of exposure to water and to irradiation were very, very short, compared with the times of exposure to weathering in the normal way. It was, of course, dangerous to draw conclusions from such short-time tests. He could only say that in all cases thus far investigated, there was correlation, but, of course, it was possible that further investigations could show differences.