APPLIED CHEMISTRY DIVISION
ORGANIC COATINGS SECTION
SUBCOMMITTEE ON TESTING PROCEDURES

HARDNESS TESTING OF ORGANIC COATINGS

Prepared for the Subcommittee on Testing Procedures of the Organic Coatings Section, Applied Chemistry Division

by

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FOREWORD

Some explanation is needed for the origin, creation and purpose of this book.

It is the work of members of the Organic Coatings Section of the International Union of Pure and Applied Chemistry, an organization that was resuscitated immediately after the last war. Since then the members, and we are only a handful, have met regularly once a year, for about three days or so, to discuss anything we like from men to molecules so long as it has a bearing on the more difficult aspects of paint technology. We hoped that the industry would take notice as indeed in some measure it has.

That therefore is the background of this book about "hardness". We, and especially the few who have had so much to do with the preparation and presentation of the material, are grateful to I.U.P.A.C. for its publication. They know that it is no display of mere erudition and neither is there any highbrow sophistication. It is an example of international co-operation in the best sense commanding the respect of all and illustrating a healthy relationship between individuals.

What has been done had a dual purpose, firstly to help those interested in the subject in a wide sense to think more deeply than before about this most difficult aspect of physical chemistry, secondly to give a comprehensive although not exhaustive, critical review of existing methods as an aid in the search for suitable procedures.

There is no invention in any of these papers. They have now merely been brought together into one volume but they are the pride of men who have given much service and time to the work. Their reward is that their efforts will be, and will be seen to be, justified especially in view of the work of the European Harmonisation Committee in setting up standards.

Broadly then, one sees how science-based industry can and must consult and use those minds which can be galvanized into creative thinking about practical things.

We inherit a mass of opinion that it is easy to accept—maybe also a mass of refuted hypotheses which are easy to set aside—but the more we are conscious of the past, the more do we see ourselves as being indebted to our heritage of knowledge. Thus will we develop sound ideas of great importance to the growth of a good public image of our work.

I am sure that my colleagues in the group, notably Mr. H. K. Raaschou Nielsen (the present Chairman) and Dr. H. W. Talen (a former Chairman) will wish to join with me in expressing our thanks to those who have made this exercise possible.

August, 1964 (the late) L. A. JORDAN†

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PREFACE

Most of the information for this publication was collected through the years 1959 to 1962 within the Subcommittee on Testing Procedures. This information consisted chiefly of individual papers that were not originally intended as parts of a booklet, but rather as a more or less systematic compilation of data and ideas. Thus, once the task of editing had been accepted, the material was treated very freely, rewritten, rearranged and supplemented when additional information was within easy reach. A measure of homogeneity has been attained in this way. Although I am aware that the information on a subject like hardness will never be entirely comprehensive, I am hoping that this booklet will be both informative and stimulating to technologists engaged in paint testing, be it within educational or scientific institutions, manufacturing or commercial enterprises or within standardizing bodies.

Many thanks are due to my coauthors. Of these I wish to mention especially Mr. Raaschou Nielsen, to whom I feel indebted for many useful discussions and his obliging assistance with numerous problems. I am also most grateful for the many linguistic corrections and other useful hints offered by Mr. Robert Hickson, Mitcham, England, as well as the stimulating criticism of Dr. K. Oesterle, Zürich, Switzerland. They are all members of the subcommittee. Finally, I wish to thank all the various contributors and above all the firm of Sadolin & Holmblad Ltd., Denmark for its invaluable support, without which this work might never have been completed.

August, 1965 P. FINK-JENSEN

CONTENTS

1. GENERAL INTRODUCTION

1.1 The concept of hardness

Most people have an intuitive appreciation of what is understood by the hardness of a material, but their conception of what actually constitutes hardness is, in general, strongly coloured by their personal experience and by their own requirements. It is for this reason that there are so many varying methods for the determination of hardness, as is clearly shown in the chapter on practical hand tests.

Similarly, the concepts generally used within different industries often deviate considerably from each other; nevertheless, they are of equal standing for they each serve their respective purposes. These different conceptions seldom have any relation to a single definite physical characteristic, but embrace a group of such characteristics. Each group results in a sort of composite property whose measurement is of value for certain materials and certain applications; but it does not resolve the relationship between the individual component elements of the composite property. It is therefore difficult to obtain a fixed general definition of what hardness actually is, and even more difficult to have it accepted universally; within a limited field, such as for example the paint industry, it may be easier.

Mott[1], citing Ashby in his book on hardness testing, regards as the best definition: "Hardness is a measure of the resistance to permanent deformation or damage". This definition appeals to many paint technologists at first sight, partly because it is an important task for them to produce paint systems that are not permanently changed when subjected to mechanical influence, and partly because test methods used for evaluation of the degree of success attained are quite generally called hardness tests. It is, however, unreasonable and contrary to general usage to demand that permanent change should always take place with hardness testing. Rubbery substances are termed hard or soft according to the ease with which they are indented, not damaged; and even paint technologists would be reluctant to accept that a brittle substance (*e.g.*, rosin) is always softer than a tough rubbery material (*e.g.*, rubber, stand oil film).

Without much argument the definition given by Braun[2] will be adopted for the purpose of this booklet: "Hardness is the quasistatic resistance to local non-homogeneous deformation caused by point or line-shaped force centres".

This definition includes permanent as well as temporary deformation of the substance. Nothing is said about how resistance should be expressed, whether as a force, an energy, a quality of the deformation tool leading to a specified result (as with the Mohs hardness scale or the pencil test), or as an amount of abraded material *etc.* Likewise the kind of non-homogeneous deformation and in particular, the amount of deformation, is not given. Thus the resistance-to-damage kind of tests are hardness tests with a specified amount of deformation, *i.e.*, the deformation leading to damage. The expression "damage" is of course by itself open to several interpretations.

The definition rules out those test procedures in which the deformation is homogeneous and not local. Accordingly tensile tests, bending tests, torsion tests and many others are not hardness tests, even if actually the same composite property is measured as with a given hardness test.

Whether one definition or another is chosen, the methods used for the evaluation of hardness each define a hardness scale, and a given material cannot unequivocally be termed hard or soft; different methods of evaluation lead to different answers. In general, therefore, it is necessary to accompany any statement about hardness by information as to the measuring technique involved.

Attempts to produce a table for conversion between hardness scales defined by means of appreciably differing methods must fail unless the choice of materia lis so limited (*e.g.*, for materials for a definite practical purpose) that in practice there appears a correlation between the various properties forming the specific characters of the materials. When such a correlation exists it is of great practical value because there is then the opportunity of choosing a convenient experimental procedure aimed at obtaining desired results.

1.2 Hardness of coatings

A particular difficulty arises in the case of coatings, which are by their very nature thin layers of materials supported by a substrate. Does hardness concern the coating alone or the system, coating + base?

For coatings on a hard base the resistance to deformation will increase with decreasing layer thickness, all other factors being unchanged. This may mean that the system, coating + base, is in practice harder, and therefore more suitable, with a thin layer than with a thick layer. Furthermore, adhesion to the base plays an important role in certain types of treatment. This is, for example, clearly reflected by the fact that a particular scratch test is sometimes called a hardness test, at other times an adhesion test. In this way hardness of a system, to all intents and purposes, becomes dependent on the inter-relationship between the individual deformation characteristics of the film and of the base, as well as on the adhesion of the layer to the base. This inter-relationship is still very little understood today. Indeed, the very concept of adhesion is rather unclear.

Paint and varnish people disregard the deformation characteristics of the base material and to a certain extent the adhesion in most cases, so that hardness is not regarded as a characteristic of a treated subject, but as a characteristic of the coating substance as a direct function of its microstructure.

However, paint films are not always homogeneous and quite often the surface is harder than the bottom layers; thus the result of hardness testing with a particular instrument is better regarded as a characteristic of the paint film, *i.e.*, of the paint substance with its particular geometry and arrangement of structural units.

The above considerations are apparently reflected in the British Glossary of Paint Terms[3], where hardness of a *paint film* is described as "the ability of the paint coating as *distinct from its substrate* to resist indentation or penetration by a hard object".

Unfortunately, more often than not, it is impossible to resolve the measured hardness into components due respectively to the film and to the substrate. This means, for example, that a comparison cannot be made of the hardness of two homogeneous films on different substrates or with different layer thicknesses. Therefore, comparison of hardness of paint films is usually restricted to fixed conditions—a fixed substrate, fixed layer thickness, *etc.*

This leads one inevitably to the conclusion that, in general, the result of hardness testing, a hardness value, is a characteristic of a painted object; only with some test methods, and with particular objects and coatings, can the value be regarded as, or converted into a characteristic of the film or—even more rarely—of the paint substance.

Apart from the special circumstances connected with the substrate and the small layer thickness, the behaviour of organic coatings is likely to be akin to that of more or less rigid plastics.

1.3 Purpose and use of hardness testing

The ultimate purpose of hardness testing is to characterize or forecast the behaviour of a coating subjected to such practical conditions as comply with the hardness definition. Accordingly, the conditions of the test procedure must usually be chosen as close to practical conditions as possible, but with the restriction that the test should be controllable in all details, yet performable within "reasonable" time and with "reasonable" resources. Usually one must compromise but it is wise to realize the aim and to choose among existing methods the one which is closest to practice. For example, it is not reasonable to expect that resistance to wear of a floor varnish could be judged by means of a Sward rocker; some kind of abrasion or wear test would be more suitable. In fact the conditions of test with the rocker and similar instruments (pendulums) do not at all resemble any practical conditions. In spite of that they are very popular, and even useful, due to their convenience of handling and the fact that they often (but not always) show a fair amount of correlation with other hardness tests, and so contribute to a preliminary general characterization of a material.

The demand for resemblance to practical conditions is of course not of equal importance to every technologist within the paint industry.

For the man who chooses and specifies materials the agreement of the measuring method with the practical concept of hardness is the only thing of real importance, but with control work one can considerably reduce the requirements to facilitate easier and quicker measurements.

In connection with research, agreement with practice is also very important as there will be created thereby a standard of measurement towards which to work; but it is just as important that hardness data and fundamental characteristics of the materials be brought, if possible, into some relation to each other. This will make it easier for the technologist to come into contact with, and to make use of, the still growing mass of accumulated experience concerning the relationships between the structure of high polymers and their deformation properties. On the other hand measurements of hardness can help in extraction of certain information about the structure of materials.

2. THEORY OF HARDNESS AND ITS MEASUREMENT

2.1 Interplay between object and deformation tool

2.1.1 Geometry of deformation

In hardness testing the object is usually subjected to forces by the action of some hard body, a tool, the shape of which differs from one method to another. For an extended object with a plane surface the stresses set up are high near the contact area and decrease with increasing distance from it; thus the major part of the movement of the sample surface is due to deformation of substance within a volume formed by a boundary surface enclosing the contact area, while more distant parts supply a negligible contribution. The shape and position of this surface depend on the kind of tool, the forces on it and the deformation properties of the sample as well as the desired accuracy of measuring. The introduction of an interface, such as between coating and substrate, will be of little influence if the coating is thick enough to enclose the boundary surface, and the movement of the sample surface will not depend on layer thickness unless the substrate is extremely deformable compared to the coating; roughly speaking this happens if the smallest width of the contact area is small in proportion to the layer thickness. However, if this width is comparable to the film thickness or larger, the interface cuts the boundary surface and deformation depends strongly on film dimensions, in so far as there is any appreciable difference between the deformation properties of the substances on both sides of the interface.

The typical example of this is the difference between a pointed tool, such as a Vickers pyramid, and a blunt tool, such as a ball, with a radius of curvature much larger than the layer thickness. At the same indentation, the former will have a much smaller zone of contact than the latter and only the properties of superficial parts of the paint film are involved, whereas in the latter case properties of the entire film, the interface (adhesion) and the substrate are significant. Hardness of the coating as distinct from the substrate can then only be determined if the properties of interface and substrate are controllable.

The details of the deformation pattern have been worked out for special cases, such as impression of a ball or a cone into an extensive body assuming Hookean elasticity or other ideal properties (Hertz[4], Gohl[5] *inter al*); however, such solutions do not apply to cases where the sphere of action of the tool includes an interface. A common feature of such theories is that the sample is thought not to adhere to the tool, so that free sliding can take place along the contact area. In practice it is not generally so, and measurements are influenced by the surface properties of the sample as well as the tool; *e.g.*, it has been found in many cases that a slight roughness of the tool apparently increases hardness because movements of the sample substance are thereby being restricted. At times the effect can be eliminated by use of a lubricating medium between tool and sample, but one has to be very careful and certain

that the sample is not impaired. Moreover, it is an artifice which may not be desirable, since it diminishes similarity to practical conditions.

Sudden changes of radius of curvature of the contact area caused by peaks or points of the tool are accompanied by high stresses in the substance under test; *e.g.*, calculations show that the stress and rate of deformation at the top of a mathematical cone are infinite. With practical tools this would lead to stress release by some kind of break, visible or invisible, unless the substance is very deformable. This last instance occurs very often, either because deformation at high stresses does not conform to the ideal laws set up for the low stress region or because the high rate of deformation leads to temperature rise and softening.

The particular circumstances at a peak may be of little consequence with many static tests, for example, indentation tests, *i.e.*, when the deformation of the substance takes place with a constantly loaded tool and leads to a kind of equilibrium with no essential relative motion between tool and substance. The reason is that even if the stresses are locally high, they only contribute little to the total reaction forces on the tool because of the small area compared to the entire contact area.

With dynamic tests as, for example, scratch tests or abrasion tests, the tool and the substance have an important relative motion; the "anomalies" at the peak may then govern the entire course of events and so determine whether a cutting, a smearing or a pulverization takes place and to what extent. Thus the hardness order of substances measured under dynamic conditions may differ radically from the order obtained under static conditions; further reasons for this are given in Section **2.2.**

Similarly the use of high loadings with blunt tools may mean a modification of the deformation pattern.

2.1.2 Statistical considerations

In the foregoing the use of small contact zones between tool and substrate was advocated to obtain measurements that are independent of the substrate, which may be regarded as an inhomogeneity of the sample; but it follows inevitably that the test becomes sensitive to possible variations in deformation properties within the film. These will cause measurements at different positions to differ unless the pattern of variation is so fine that the above mentioned boundary surface includes an adequate statistical representation of all structural units within the sample. In this case the hardness is well defined in a statistical sense and the result should be taken as a statistical mean. If the pattern is coarse, a single measurement will not represent the properties of the whole sample and has no significance; a meaningful single hardness value can only be obtained by averaging of many results; a measure of inhomogeneity is then concurrently obtained through the statistical distribution of hardness values about this average. An alternative would be to use many tools at the same time and evaluate the total effect; this is actually done with some abrasion tests.

The considerations are not only of academic interest; in fact many paint films, whether pigmented or not, turn out to be lacking in homogeneity, much more so than is generally expected. The defect may have various origins; however, two common causes are non-compatibility of resins and flocculation of pigments.

2.2 Deformation of polymer materials

2.2.1 Viscoelasticity

Since hardness is defined by the methods used for its determination, "Theory of Hardness" is rather a collection of theories with one common feature—deformation of matter. It is thus reasonable to review some fundamental properties of polymer materials which are determining factors in hardness measurement.

The vehicle, the most important part of the paint film, has, like all other materials, a certain instantaneous elasticity due to bending and stretching of valency bonds. This elasticity, usually Hookean in character, has a high elastic modulus of the order of 10^{10} dyne/cm^2 (steel $= 2 \times 10^{12}$ dyne/cm^2) or 100 kg/mm^2. If this general elasticity alone is present, the material will have a small elongation at break and will be brittle.

This instantaneous elasticity is symbolized in *Figure 1* by the spring, *A*. Deformation and recovery take place instantaneously on loading and unloading.

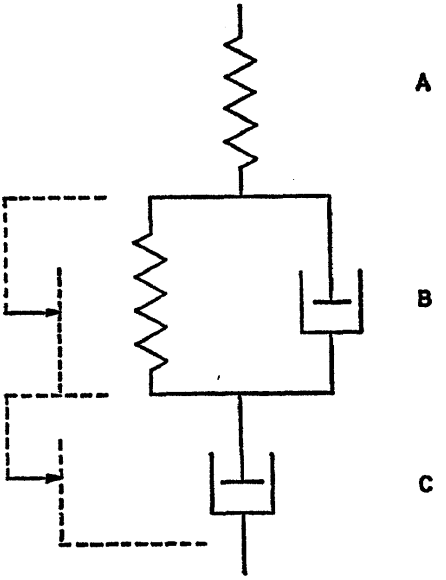

Figure 1. Rheological model of a polymer material

Usually a second type of elasticity is also present, a retarded elasticity. This can be symbolized by the Kelvin element *B* in *Figure 1*, *i.e.*, a spring in connection with a viscous resistance to movement, a dashpot. This system will only gradually come to equilibrium on loading, and with unloading it will recover only gradually to its original state.

This latter type of elasticity is due to uncoiling, disentanglement, and partial alignment of the molecular chains, interconnected, for example, by cross-linking or by crystallites. Very large deformations are attainable due to this uncoiling of molecular chains, *e.g.*, vulcanized rubber can be extended by 1000 per cent.

Thermal agitation will always tend to randomize the molecules and therefore constitutes an elastic resistance to the deformation that will tend to derandomize by alignment of the molecules. Here the corresponding elastic moduli are normally of the order 10^7 dyne/cm^2 or 0·1 kg/mm^2.

Since deformation implies mutual displacement and interchange of chain segments, and not just a small atomic displacement, it is conceivable that available time is one important factor governing the deformation process.

On loading or unloading, approach to equilibrium takes place exponentially and can be characterized by a time constant τ, the retardation time, giving the time during which the displacement from equilibrium decreases to a fixed fraction ($1/e = 1/2{\cdot}718$) of the original displacement.

This implies, roughly speaking, that the application of loads for a much smaller time than τ has a negligible effect, while for times greater than τ practical equilibrium prevails. τ depends formally on the ratio between the viscosity and the elastic modulus of the *B*-system. With increasing viscosity the retardation time increases. τ is a quantity which may have values from fractions of a second to years.

If the material is not cross-linked, or if the bonds connecting the molecular chains can break and reform, the chains may slip over each other and so give rise to flow of the material and a permanent set (no recovery on unloading). This flow is characterized by a viscosity and is symbolized by the dashpot *C*. True flow does not usually occur with coatings.

This full model successfully explains the phenomena of instantaneous elasticity, retarded elasticity and flow of polymer materials.

The behaviour of the model under a given load is shown in *Figure 2*. The compliance *J*, defined as the ratio of the amount of deformation to the stress applied, *i.e.*, the reciprocal of the modulus, is given as a function of the duration of the loading.

If the duration is short compared to the retardation time τ, only mecha-

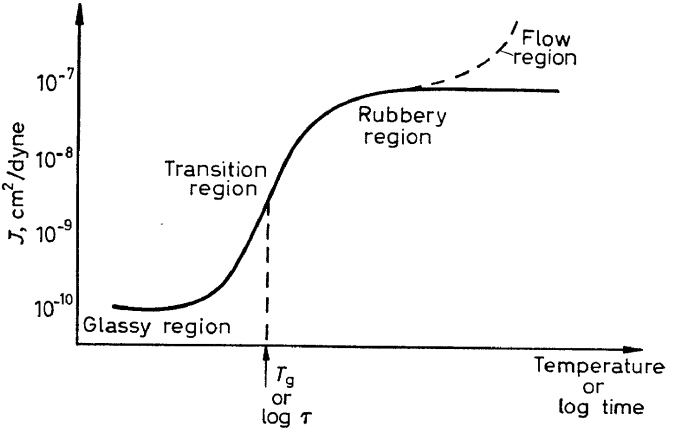

Figure 2. The dependence of the compliance *J* of a polymer material upon time or temperature. τ = retardation time; T_g = glass temperature

nism A responds (glassy response) so that J is about 10^{-10} cm^2/dyne. At times somewhat larger than τ mechanism B comes into play and J is raised to about 10^{-7} cm^2/dyne, and at still larger times flow may become important due to mechanism C.

Since the behaviour of the polymer as described by the model depends on the relative values of loading time and retardation time τ, a systematical decrease of τ at constant loading time will have a similar effect as the increase of time at constant τ. Thus increase of temperature has the same effect as increase of time under load (*Figure 2*) since a rise in temperature means decreased viscosities η_B and η_C and decreased τ. The parallelism between the effects of time and temperature is so extensive that certain mathematical relationships hold for amorphous materials, such as are many coating materials.

However, if the polymer is partly crystalline the principle does not necessarily hold because the presence of crystallinity will mean that the degree of cross-linking can change with temperature.

Thus at high temperatures (*Figure 2*) the polymer material is essentially a liquid in which deformation is due solely to flow, provided it is not cross-linked. At a somewhat lower temperature C stiffens, whilst the retardation time still remains smaller than practical times (*i.e.*, seconds or minutes). This means that mechanism B predominates, the material exhibits rubber-like elasticity and is rubbery.

On further cooling τ increases to beyond practical time limits, the material becomes more leathery, and finally a certain temperature is reached at which mechanism B ceases to have any significance, leaving deformability to mechanism A alone.

The region between 10^{-7} and 10^{-10} cm^2/dyne is the transition region. For amorphous polymers the temperature corresponding to the central point of this region is within a few degrees of the glass-temperature (defined as the temperature at which an abrupt change of coefficient of expansion takes place). The glass-temperature is governed by the entire molecular structure of the material. Most coating materials at room temperature belong to this transition region, in particular to the low compliance part of this region. As an example may be quoted the 30/70 butadiene–styrene copolymer which has a glass-temperature of 18°C.

The picture given is oversimplified in many ways. It usually appears that one mechanism B is not sufficient to satisfy the data but that several Kelvin elements with differing retardation times are necessary. Thus, often, the structure is given by a retardation spectrum, a curve showing how the elastic compliance is distributed over the retardation times. Such curves often show peaks, indicating grouping round discrete retardation times. A retardation spectrum can be obtained by detailed analysis of a creep curve, *i.e.*, the analysis of the elongation with time of a film strip under constant tensile stress (*Figure 2* may be regarded as a creep curve). A few experimental creep curves[6] are given with full lines in *Figure 3*; from such measurements it was found, for example, that the behaviour of a particular stand-oil film could be described by one retardation time of less than 0·5 sec (mechanism B_1), one very pronounced of about one month (mechanism B_2), plus a viscosity of about 10^{14} poises (mechanism C).

2.2.2 Plasticity

A much more serious objection to the picture given by viscoelastic models is that it is only valid if the applied stress is small in comparison to the ultimate strength of the material. At high stresses new phenomena make their appearance, in which the materials, when a certain stress range is surpassed, show so-called "cold flow". This defines more or less sharply a yield value or yield stress and the behaviour of the material approximates to that of metals, although the detailed mechanism is probably very different.

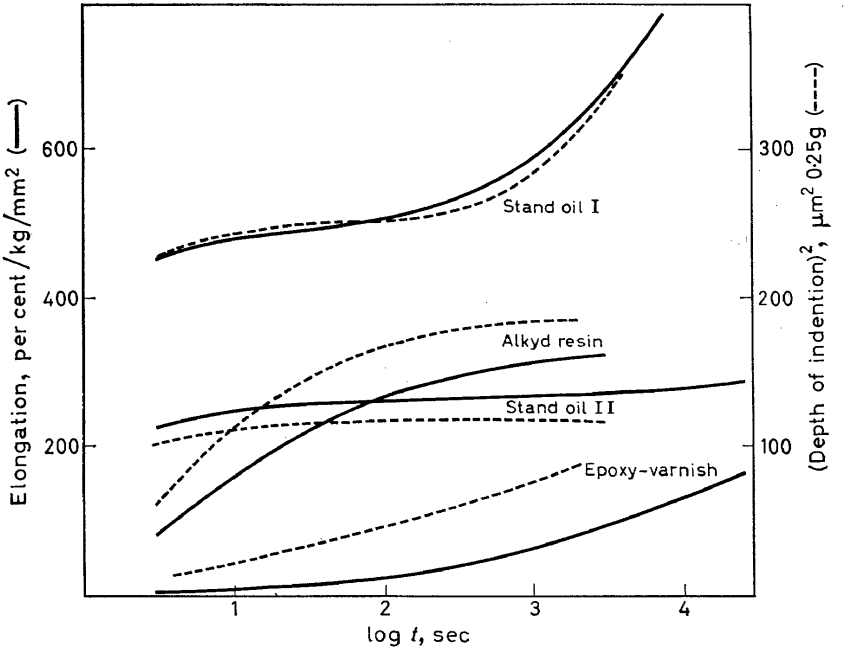

Figure 3. Experimental curves as derived from usual creep tests (full lines) and indentation test (broken lines)

This can be symbolized by a solid friction in parallel to mechanism *B* and/or *C* as shown with dashed lines in *Figure 1*; the mechanism to which it is attached cannot function unless the stress exceeds a certain value (yield stress) corresponding to the solid friction present.

The flow observed in this plastic range is frequently irrecoverable and so constitutes true flow. In other cases the substance shows "elastic memory"; *i.e.*, there is recovery of shape if the temperature is sufficiently increased. In this case the solid friction should be placed at *B*.

The causes of the behaviour are not entirely known and are probably not always the same. It may be due to the scission of valency or molecular bonds which may or may not be reformed in new positions, to the overcoming of steric hindrance or to the effect of heat evolved during the deformation process upon strongly temperature-dependent elastic and viscous properties.

It is obvious that whatever the cause, cold flow will in practice only be important when high stresses are easily created within the material. A fixed

amount of deformation will create the higher stresses the less mechanisms B and C are involved, *i.e.*, the smaller the relaxation time and the higher the glass-temperature.

The yield value itself may depend on the amount of deformation. If yield value increases with deformation it is a case of work hardening, which, incidentally, may be due to alignment of chains and accompanying crystallization. If stress or deformation is high enough, the material will break down by rupture which may or may not be preceded by yielding. Neither yield value, ultimate strength nor deformation are constant properties; they are like the other mechanical properties mentioned, temperature—and rate-dependent. Yield value and strength increase with decreasing temperature or duration of test while ultimate deformation decreases. The sensitivity to these factors is highest in the transition region or—to the paint technologist—the coatings region between the rubbery and the glassy state.

2.2.3 The effect of pigmentation

If the coating contains pigments or extenders, the properties of the vehicle are modified. Hard, inert particles give a stiffening effect (decrease of J), partly because of decrease in deformable material per unit volume, and partly because the detailed deformation pattern is changed. At low concentrations of inert spherical particles, J can be calculated from volume concentration c and J of the vehicle by theoretical formulae such as that of Guth cited in reference 7:

$$\frac{1}{J} = \frac{1}{J_0}(1 + 2{\cdot}5\,c + 14{\cdot}1\,c^2)$$

In this case retardation times are unchanged.

Such formulae are of little value with surface coatings, because volume concentration is often too high, particles are not spherical or perfectly dispersed and above all, the inertness is usually, at the least, questionable. The pigment may react chemically with the vehicle or selectively adsorb parts of it. It may also change the rate and character of the drying and aging processes and modify the microstructure of the vehicle by orientation phenomena *etc.*; such phenomena cannot be accounted for in any simple way.

For similar reasons very little general information is available regarding the behaviour outside the stress region within which viscoelastic theory applies. With low volume concentrations strength values tend to increase with pigmentation in approximate proportion to the increase in elastic modulus, while elongation values decrease somewhat[8].

2.3 The interplay between base, film and tool in some important cases

The properties referred to in the previous section are more or less important in any test of the mechanical properties of coatings, and thus also in hardness tests. As mentioned at the beginning of this chapter different hardness tests differ in their choice of such properties; these tests can thus be grouped according to this choice, *e.g.*: (*i*) tests in which rupture is an inherent part of the procedure; (*ii*) tests in which rupture need not occur.

Very little fundamental knowledge is available regarding tests (*i*); the

situation regarding tests (*ii*) is a little better. As examples certain indentation tests, damping tests and scratch tests, the principal features of which reoccur in many similar tests, will be considered.

2.3.1 Indentation tests

In indentation tests a suitably shaped body, the indentor, is forced against the paint surface for a certain time (*e.g.*, 30 sec) and the load is then removed.

It is the depth of indentation or the size of the indented mark at suitable times before or after unloading that is observed. A Vickers diamond (a square pyramid with 136° between opposite sides) is often used, as is also the Knoop pyramid (*see 3.1.1*). They will behave in much the same way, and the following applies only to pyramidal or conical shapes.

For elastic bodies obeying Hookes law, the depth of indentation i is related to the applied load P and the elastic compliance J (reciprocal elastic modulus) by the formula:

$$PJ = \text{const.} \times i^2$$

provided that i is sufficiently small compared to the coating thickness, so that the influence of the coating–substrate interface can be neglected. With the Vickers diamond i must then be less than 10 per cent of the coating thickness (van Laar[9]). If an area of indentation is determined rather than i, this area replaces i^2 in the equation but with another constant. For viscoelastic films, use of the equation will give J values that depend on time at constant temperature or on temperature at constant indentation time, in a similar way to the creep in *Figure 2*. As an illustration of this, *Figure 3* shows a comparison between creep curves obtained in the usual way by loading of film strips and by indentation measurements with a Vickers diamond.

Thus it is possible to arrive at distributions of retardation times from indentation curves and vice versa. The constant in the above equation is of the order of 3 for a Vickers pyramid, but will vary somewhat according to the particular characteristics of the material, *e.g.*, whether sliding along a pyramid face is free or restricted.

After removal of the load the deformed elements of the film will return to their original state and the impression disappears completely unless flow (mechanism C) has taken place. As mentioned above true flow does not occur with cross-linked materials. If the material can be adequately represented by a model containing only retardation times less than the loading time, the impression will disappear in much the same way as it was created. A plot of J (calculated on original load) against time after unloading will be very similar to the reversed curve of J against time during the impression period, as shown in *Figure 4*(*a*).

If, however, longer retardation times dominate, this will not be the case; recovery is slowed down and will in case of flow (*i.e.*, infinite retardation time) never take place, as shown in *Figure 4*(*b*). The remaining J measured a fixed period (equal to or longer in duration than the time under load) after unloading is essentially a measure of the number of processes with retardation times greater than that of the period under load.

The indentation process is here described as being analogous to the creep

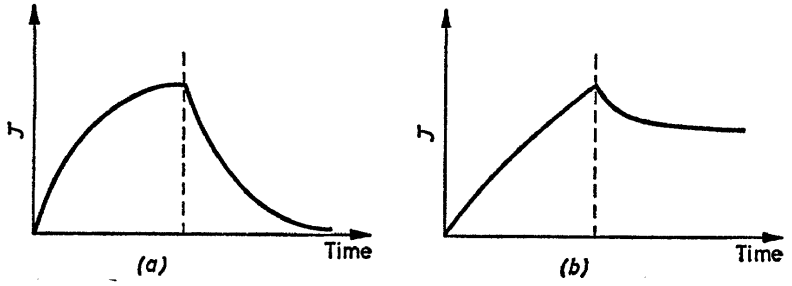

Figure 4. The behaviour of J (*see* p. 259) during an indentation test with loading and unloading in two cases

test, where no yield value is exceeded because of the low constant stresses applied. With a Vickers diamond indentation test the state of affairs is actually somewhat different, since at the first moment of touch the load per unit area is at least theoretically infinite. If rapid elastic processes can take place such as when the material is rubbery (*i.e.*, low glass-temperature) this is not important because the area of contact is very rapidly increased and the stress accordingly decreased. Thus the whole process is governed by elastic and viscous phenomena. With increasing glass-temperature, however, the principal sources of elastic and viscous compliance (mechanisms B and C) are removed and stress will remain at a high level until, by cold flow or other non-linear processes, it reaches a load per cm^2 corresponding to the yield value. Further deformation is again governed by elastic and/or viscous processes. If the indentation is governed chiefly by a yield value θ this can be calculated by a formula:

$$P = \text{const.} \times \theta\, i^2$$

Thus, we may have to deal with two different mechanisms, one with a low glass-temperature and one with a high glass-temperature and a transition region.

This last instance is exemplified by the epoxy-varnish of *Figure 3* where the correspondence between creep curve and indentation curve is actually very bad in spite of their graphical proximity and similarity. At short times (some seconds) the "hardness creep" exceeds the normal creep by a factor of 10. If, however, this initial plastic deformation is subtracted, the agreement is much improved.

Yielding of the coating, like viscous flow, leaves an impression which will never disappear. The impression is, however, normally much sharper in outline, and, if elastic processes are not completely absent, the indentation mark is evident as a square with sides bulging inwards. In the case of only slight yielding, this mark eventually reduces to the diagonal cross. The reason for these shapes is that the stresses produced under the pyramid during indentation are not uniformly distributed, *i.e.*, they are much higher along the edges of the pyramid than along the faces, and as a consequence yielding is more pronounced along the edges. Should yielding be accompanied by work hardening, the square sides may bulge outwards.

The pyramid hardness test can be safely applied to films on undercoats

provided that these are not softer than the top layer, and indentation into the top film is small.

Sometimes a steel ball is used as an indentor; but it is usually not a good choice for surface coatings. The front of this indentor is almost parallel to the coating and the contact area is a circle with a radius comparable to, or larger than, the layer thickness.

Consequently the restricting influence of the substrate cannot be neglected as with the pyramid. According to a theoretical calculation[10] depth of indentation will vary with layer thickness to a power between 1/2 and 1; with load to a power between 1/2 and 1/3 and with ball diameter to a power of $-1/2$ to $-1/3$. The latter dimensions are easily controlled, but for layer thickness it may, at times, be difficult. To get a measurable indentation, one must apply much higher loads than with a pyramid and disturbing deformation of the substrate may occur. Measurements obtained on films with undercoats are characteristic of the entire system, not only of the top-coat. On the other hand this may at times be of advantage.

2.3.2 Damping tests

Familiar tests of this type are the rockers (Sward or others) and the pendulums (Persoz, König-Albert, *etc.*), in which a loaded ring, cylinder or ball performs a reciprocating, rolling movement on the paint surface. The consumption of energy per swing expressed by the number of swings, or the time necessary to decrease the amplitude to a certain fraction is the measurement made. This energy is spent in deformation, but the detailed deformation pattern is very complicated. The test could be regarded as a rolling friction experiment and a vibration test; a rolling friction experiment because of the rolling movement and a vibration test because of the reciprocating movement. Here the damping test will be regarded as a rolling friction experiment and for simplicity it will be assumed that the material can be represented by a single retardation time.

The rolling ball indents the surface (*Figure 5*), setting up a pressure distribution below the ball counteracting the weight of the ball. The

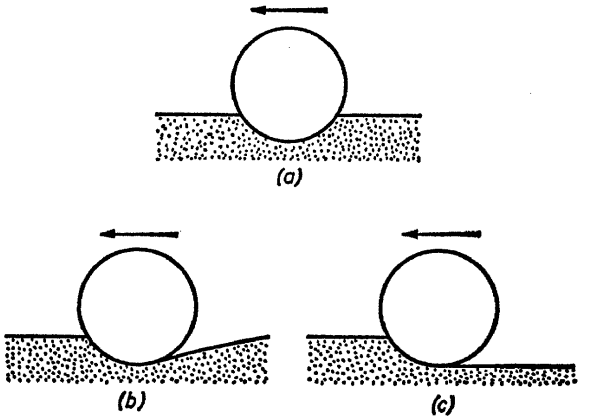

Figure 5. Cross-section of a ball rolling on the surface of (*a*) a Hookean material; (*b*) a viscoelastic material and (*c*) a viscous material

pressure in advance of the centre creates a moment constituting a resistance to the movement, while the pressure of contact behind has the opposite effect. Thus the total resistance will depend on how the pressure is distributed under the ball, and it will be larger, the broader and more unsymmetrical is this distribution. If the material deformed in advance of the ball can recover more or less completely within the time it takes for the ball to pass the indentation, *i.e.*, with elastic behaviour, and small retardation time, the pressure distribution will be almost symmetrical (*Figure 5a*). At the same time the depth of indentation is determined by the elastic compliance of the substance. Accordingly resistance will be small but will increase the slower is the recovery of the material (*i.e.*, the more the retardation time approaches the passage time) because of decreasing symmetry (*Figure 5b*).

If the retardation time is long, the behaviour is viscous, very little recovery will take place (*Figure 5c*), and the pressure distribution will have a maximum lack of symmetry. However, the indentation is now no longer determined by elastic but by viscous forces. Lack of available time does not allow the ball to sink into the material, so that the resistance will be small because of the narrowness of the pressure distribution, and will increase with decreasing retardation time.

Thus resistance will be at a maximum when passage time and retardation time of the substance are of equal magnitude. Substances with higher as well as lower retardation times will show greater damping hardnesses. This is confirmed experimentally by the fact that soft vulcanized rubber is very "hard"[11] and moreover by experiments demonstrating that damping hardness may show a positive temperature coefficient[6].

The situation is blurred somewhat by the reciprocating movement and by the variation of the rolling velocity. If the damping test is regarded as a vibration test the same final features emerge qualitatively.

Some mathematical theory of rolling friction applying to substances in bulk has been published[12, 13]. For coatings it emerges that layer thickness is an important factor[11, 14] and that different coatings exhibit different dependences on thickness. Calculations[10] show, that with low retardation time and elastic response, damping should be independent of layer thickness as long as the substrate can be regarded as stiff. In the case of a long retardation time and almost viscous response damping should vary with layer thickness to the power 0·6. Thus the pendulum hardness should be proportional to the layer thickness to a power between zero and — 0·6 according to the rheological properties of the coating in question. This is in excellent agreement with the experimental results of Wapler[11], who found that the hardness ratio of films of 28 μm and 52 μm thickness lies between 1 and 1·5 for various substances, while the theory predicts the interval 1 to 52/28 to the power 0·6, *i.e.*, 1 to 1·45.

The actual results obtained with a particular apparatus depend of course on the detailed construction of the apparatus and also to some extent on the character of the surface of the film. Nevertheless, there is a rather close correlation between results obtained with different rockers and different pendulums, and approximate conversion can be made.

However, one should not rely on such a conversion, without experimental verification with the particular kind of substance.

2.3.3 The indentation test compared to the damping test

The rolling ball test can be roughly regarded as consisting of two phases, (*i*) an impression period in advance of the ball and (*ii*) a following period, in which the instrument "examines" whether or not recovery takes place within a time equal to the impression period. This is, however, exactly the procedure followed in an indentation test, when the remaining indentation after a loading period and a period of rest is determined. One would therefore expect to get similar results in spite of differences in the detailed deformation pattern. However, the methods differ in one important respect. While the indentation test usually lasts about a minute the corresponding time in the damping test may be perhaps 1/50 sec. The significance of this is that the relationship becomes obscure.

2.3.4 Scratch tests

Scratch tests appeal to many paint technologists because resistance to scratching is a requirement which occurs in connection with almost any type of finish. Correspondingly a multitude of instruments have been developed with these common features: a loaded tool of suitable shape (ball, stylus, pyramid, knife *etc.*) is drawn across the coating with controlled, constant or variable velocity. It is the amount of damage caused by a fixed load that is examined, or the load necessary in order to obtain a certain amount of damage. At small loads and with blunt tools one expects the behaviour to be very similar to that described for a rolling ball; a track is created which, according to the prevailing viscoelastic properties, will disappear at a slower or faster rate; or, in the case of true flow, will remain. Thus an evaluation of the size of the groove is analogous to the measurement of remaining indentation in an indentation test with very small loading time.

With sharp tools, high loads and fast movement, large stresses are set up in the film and ultimate properties such as yield value, strength and others become of increasing importance, in particular when, as is often specified, the load is so high that the base is revealed.

The mechanical energy spent in deformation is transformed into an appreciable amount of heat, which cannot dissipate completely by conduction during the short period of deformation. Thus the results do not refer to the constant temperature of the undeformed material, but rather to an unknown temperature range. If the mechanical properties of the film are strongly dependent on temperature an apparent yield value can result as mentioned in section *2.2.2.*

Adhesion to the tool sometimes plays an important role, evidenced by the fact that hardness values may be changed considerably by lubrication. Likewise variations in adhesion to the base and in layer thickness result in varying hardness values.

From a theoretical point of view the behaviour grows exceedingly complex. With limited ranges of material results can sometimes be correlated with results from damping or indentation tests[15] but in general it is impossible, even approximately, to derive the scratch resistance from other hardness values[11]. The scratch tests have merits of their own.

3-4. HARDNESS TESTING METHODS

General information

Generally speaking, test results that cannot be reproduced or at least compared with other measurements are worthless. In hardness testing many factors of different kinds are involved all of which must be under control, although it is sometimes very difficult to ensure this. Thus temperature and humidity are important variables and hardness measurements, like all other mechanical tests on paint films, should be performed under constant atmospheric conditions, *e.g.*, in a constant temperature and humidity room[11]. All the methods are to a greater or lesser extent sensitive to changes in deformability of the substrate, layer thickness, roughness and tackiness of the sample surface, relative size of inhomogeneities and contact area with the tool, and some also to adhesion to the substrate. Their quality may, from a theoretical and scientific point of view, be paralleled to the degree of insensitivity to such factors. From a more practical viewpoint, the conditions under which the coating has to serve are often so variable, that this factor outweighs a considerable amount of inaccuracy in the measuring procedure and lack of control of the above factors.

The measuring methods to be mentioned are divided in two groups:

(*i*) instrumental methods;

(*ii*) hand methods.

Hand methods are here defined as procedures that can be performed entirely without instruments or with instruments that are considered to be available to anyone, *e.g.*, coins, pencils.

Along with the descriptions and discussions the more important contributions to relevant literature are reviewed.

It is sometimes important whether a test should be regarded as destructive or non-destructive; the judgment will, however, be different in different cases. Broadly speaking, only the damping methods and some of the indentation methods are non-destructive in the sense that no readily visible and permanent mark is left.

Literature

General treatments of hardness testing procedures are given in the two important books on paint and varnish examinations by Gardner[16] and Wilborn[17] in which many instruments and methods are described; on the whole, however, an appreciation of the methods is lacking. A short review of mostly older literature is given; such literature is only mentioned in this booklet with reference to these books. There is available a useful and fairly comprehensive account of various kinds of hardness tests for coatings along with some appreciation[18]. Literature of a more specific nature is referred to in the appropriate paragraphs.

3. INSTRUMENTAL METHODS

In the description of methods and instruments, working principles have been stressed without going into fundamental questions; no definite working procedures are given, as different lines of action may be suitable in different cases and standardization has not proceeded very far yet.

The methods have been arranged in groups according to the measuring principles: indentation testing, damping testing, scratch testing and abrasion testing.

Representative apparatus of each class is referred to in the report of SVMT[2] along with hints for useful measuring techniques with various materials—not specifically organic coatings.

The book of Mott[1] gives an almost complete review on micro-hardness testing and the instruments required (except that plastics and paint films receive only brief attention), and on the deficiencies that arise in test procedures from instrumental defects. Thus the results of hardness testing and the interpretation of results are influenced by many factors, *e.g.*, vibrations, duration of application of load, shape of indenting tool and means of measurement of indentations—all of which concern the instrument. Other factors arise from the material itself, as from the preparation of the material and its orientation in relation to the indenting tool, from directional characteristics due to cold working, elastic properties and local hardness variations. The chapter dealing with the sources of faults and the influence of the different factors briefly indicated above is large and one of the most important in the book.

3.1 Indentation tests

3.1.1 General

The indentation test consists of forcing a suitably shaped indentor against the paint surface and observing some suitable geometrical characteristic of the ensuing deformation of the film substance.

The hardness testing apparatus is designed to apply a load to the indentor for a certain time and measure the film deformation either under load or after unloading. Measurement under load after a fixed time allows the determination of a hardness value only, while an additional measurement at a fixed time after unloading roughly speaking affords information as to the relative importance of viscous and elastic processes in the case under investigation. If viscous processes prevail, the mark never disappears, while it disappears completely sooner or later if the response is purely elastic. This has been commented on in details in the theoretical chapter (*2.3.1*). The instrument should preferably be adaptable to both kinds of measurements.

Indentors.—The shape of the indenting body is always chosen in such a way that the contact area increases with increasing penetration depth. So far only a few shapes have been used in connection with paint films.

Pointed tools: Vickers pyramid is a square base diamond pyramid with an

angle of 136° between opposite faces; it was originally designed for metals. The Knoop indentor is a pyramidal diamond with included longitudinal angles of 172·5° and included transverse angle of 130°. The ratio of the long to the short diagonal of the impression is approximately 7 : 1.

There is really no special reason to insist on a pyramid; a cone as recommended by Kuntze[19] might do just as well; apparently, however, nobody has ever applied it to coatings.

Sharp tools: A truncated double cone, *viz.*, the sharp edge is the circumference of the common circular basis of two identical cones.

Blunt tools: Steel balls of suitable diameter.

The depth of indentation obtained with a fixed load depends on the layer thickness of the film, the variation being more pronounced the flatter the apex of the indentor (*see 2.3.1*). The pointed or sharp tools are thus more advantageous for paint testing than balls in spite of the discontinuity of stress distribution at the apex of the pyramid. With plastics, when thickness is less limited, a ball is preferred[5]. The influence of layer thickness in the case of the Vickers pyramid is demonstrated in *Figure 6* by measurements on a

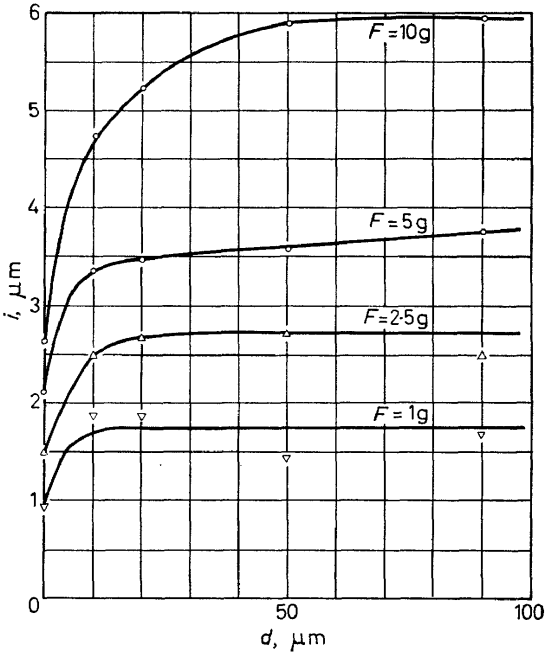

Figure 6. An example of the dependence of indentation depth i upon layer thickness d and load F for a Vickers pyramid. (After van Laar [9])

particular film by van Laar[9], who concludes that indentation should not exceed one twelfth of the film thickness. Similar results were obtained by Wapler[11] who showed that withindent ation below 3–4 μm the results with 28 μm and 52 μm films did not differ significantly. This also corresponds to the results of Gusman[15] with the Knoop indentor.

With high indentation each coating will show an individual behaviour as to the dependence on film thickness; even with small indentations apparent anomalies may arise due to lack of homogeneity of the film.

The characteristic observed could be indentation depth or the area of contact with the tool. While indentation depth under load could easily be determined with appropriate instruments, it is at best very difficult to determine the contact area under similar circumstances; accordingly measurement of indentation depth affords the most possibilities of obtaining information about the substance under test, allowing a separation of viscous and elastic properties. With indentors having sharp edges it is sometimes possible after unloading to observe the maximum size of the impression, because the film substance does not recover completely from the heavy strain at the edges; some vague idea of the relative importance of viscous and elastic processes can then be deduced from the shape of the mark left (*see 2.3.1*) but it does not work generally. An elegant procedure due to Grodzinsky[20, 21] involves silvering of the surface to make the maximum area under load visible after unloading. The Knoop diamond and the truncated double cone as used by Buchholz[22] both lend themselves very well to microscopical measurement of the impression as they afford a long, relatively easily measured mark.

Application of preload.—The measurement of small indentation depths (0–10 μm) is complicated by difficulties with the precise determination of zero point, *i.e.*, the point corresponding to touch between indentor and surface. As indentation is proportional to something like the square root of load (*see 2.3.1*) even a small force may cause a measurable indentation, and erroneous readings. The importance of such errors depends on constructional features and increases with decreasing hardness of the coating. To avoid the doubtful zero point it is sometimes useful to apply a small preload and consider the resulting position of the indentor as the zero point.

Although of advantage to the measuring procedure the hardness figures described below are no longer independent of the main load, even with pyramids and cones, unless the preload is chosed as a fixed fraction of the main load; this has not been practised but would be a very sensible thing to do.

Reporting of the results.—According to the indentors applied and to particular requirements the results could be treated in different ways. The straightforward choice is to give hardness as load per unit area of the mark (with microscopical measurement) or per unit area of the cross-section of the indentor in the plane of the original coating surface; this last area is easily calculated from measurements of indentation depth. Alternatively the reciprocal value could be given as a measure of softness. With indentation measurements such values could be given under load and after unloading, characterizing viscous + elastic and viscous hardness (softness) respectively.

In case of pyramids or ordinary cones, these figures are almost independent of load applied and layer thickness if the indentation does not exceed about 1/10 of layer thickness. This does not apply to other indentor shapes and the conversion mentioned loses its real meaning. To make hardness comparisons possible, layer thickness and load must then be specified and the indentation recorded, or layer thickness and size of indentation are specified and the appropriate load determined by interpolation or extrapolation.

In principle the same procedure has to be followed with pyramids if the indentation exceeds a tenth of the layer thickness or a preload is used for the zero adjustment, unless the preload is negligible in comparison to the main load.

3.1.2 Apparatus

The greatest difficulties of construction are undoubtedly caused by the rather trifling thickness of the paint films, necessitating refined apparatus of relatively high cost for the measurement of indentation; yet, since older types using microscopic measurement of the indentations are not suitable for coatings, essentially only such instruments will be reviewed which permit measurement of the indentation depth under load.

The application of the load must be made in such a way that the force is not increased by inertial forces above the weight of the load, and a vibration-free installation is necessary.

The first three instruments mentioned below (TNO, Vught and Wallace) all work on the same principle, *i.e.*, by means of a micrometer screw, or similar device, measurement is made of how far the sample has to be displaced to bring the loaded indentor back to its position when unloaded (or preloaded). Deviations from this position are detected through changes of electrical capacitance between two condenser plates, one being mechanically coupled to the indentor and the other fixed.

The TNO hardness tester[23] developed by Brunt consists of a test head which replaces the objective on a microscope stand. The sample is placed in a horizontal position below it. A Vickers pyramid is mounted at the bottom of a small frame of plastic material, which carries a surrounding cone of aluminium sheet and, on the top, the support for the loads. The cone is surrounded by another metal cone fixed to the test head. The frame is movable in the vertical direction guided by a vertical supporting pin sliding in a ruby bearing. The relative position of the two cones can be read from a capacitance meter indicating the capacitance between them. The head is lowered to such a position that the pyramid and the frame rests on the coating with a preload of 0·5 g, and the capacitance meter indicates a standard capacitance between the cones. The load is then applied by means of adjustable weights within the test head (0·5–25 g); the head is lowered again by adjustment of the micrometer screw until the meter shows the standard capacitance. The correction in height equals the indentation depth. After unloading, the resilience is determined in a similar way. The limits of error using this device are $\pm$ 1–2 μm which is not good, because of the unstable equilibrium of the above-described load support frame when standing on the coating. To retain an indentation depth below 1/10 of the layer thickness as well as a reasonable accuracy, the film thickness will have to be 0·1–0·2 mm.

The Vught indentation tester (*Figure 7*) developed at Philips has repeatedly been described in the literature, but van Laar[9] gives the most detailed description of how to apply the device for testing coatings.

The sample is clamped with the coating downwards to a movable platform and the Vickers pyramid mounted on the end of a rod can be pressed against the coating from below through a hole in the platform. The vertical

rod is supported by two horizontal leaf springs and a known force can be applied to the rod and the indentor with a spring, the tension of this being adjusted by means of weights. A condenser plate attached to the rod extends into the gap between two fixed plates and all three plates are connected to a Philips capacitance bridge (a Wheatstone bridge) which indicates any deviation of the indentor from the zero position. The platform can be displaced with a micrometer screw and a system of lever arms without free play (accuracy 0·1 μm) and the indentation depth is determined as the distance the platform has to be moved to balance the bridge again after application of the load to the indentor.

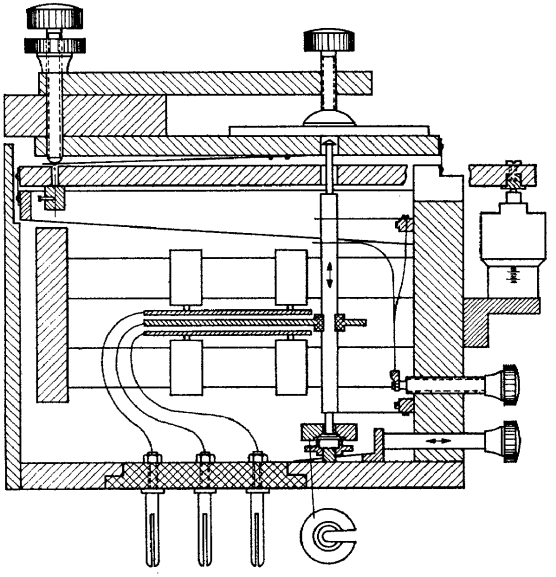

Figure 7. The Philips Vught indentation hardness tester. (After van Laar[9])

The accuracy of the mechanical installation is very high and the indentation depth is measured to about 0·2 μm, which is satisfactory for films of normal thickness. Some inaccuracy may arise from difficulties in obtaining the correct zero point.

The Wallace electronic indentation tester[24] operates on similar principles to the two preceding instruments. The indenting tool touches the coating from above and is loaded by weights. The desk supporting the coated panel is displaced vertically by means of a wedge sliding horizontally on another wedge. The level of the indentor is indicated either optically (magic eye) or acoustically (ear phone) by the beat frequency of two oscillating electronic circuits. One of these contains the variable condenser, which is mechanically coupled to the indentor.

There are different versions of this apparatus existing; with the one suitable for coatings it is possible to work with an accuracy of 0·3–0·5 μm. A description and criticism of the instrument is given in reference 25.

The first pneumatic indentation tester was made by Grodzinsky[26, 27], but because of the large preload of 7g it was not suitable for coatings. Recently, however, Monk and Wright[28] described a similar instrument (*Figure 8*) which they have used successfully with coatings for some years.

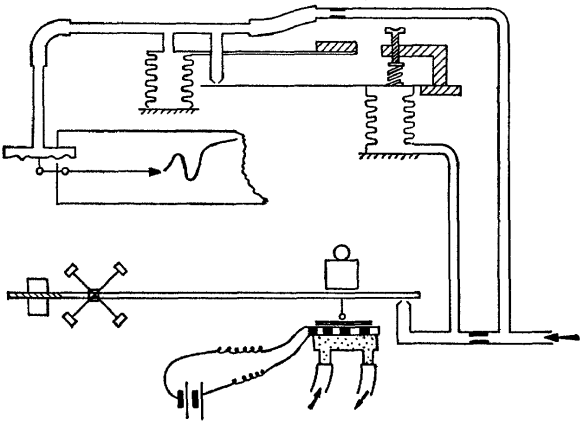

Figure 8. Pneumatic micro-indentation hardness tester. (After Monk and Wright[28])

The indentor is connected with a flat plate, the distance of which from a fixed orifice changes during the indenting procedure causing an air stream from the orifice to change. The resulting varying back-pressure towards the air supply is amplified and utilized to activate a pneumatic recorder, that plots the indentation depth or the recovery. Full scale deflection corresponds to 6 μm. The indentors are ball-ended needles with diameters from 0·06 mm to 1·6 mm; presumably other shapes could be used too.

A unique feature is the incorporation of a Frigistor unit, a Peltier effect device, which can bring the specimen to any temperature between — 20°C and 90°C in a few minutes, which allows one to obtain much faster and more complete information about the rheological properties of the coating (*cf. 2.3.1*).

The Tukon micro-hardness tester[29] utilizes the Knoop indentor (*3.1.1*). In operation a button is pressed and the instrument executes a series of automatic operations. The indentor is impressed into the coating at a fixed rate of loading, the load preset by the operator is applied for a fixed length of time, and finally the indentor is removed from the coating. The length of indentation is then immediately measured with a microscope attached to the instrument. The Knoop indentor affords conveniently long marks. When used according to ASTM D 1474-62 T the time under load is 18 sec.

With the Pfund method[29], which is also described in ASTM D 1474-62 T, it is possible to make measurements under load, as the indentor is a transparent quartz or synthetic sapphire hemisphere, allowing observation of the contact circle through it; the diameter of the sphere is 0·25 in.

The Buchholz indentation tester[22] which is standardized in Germany (DIN 53153) is a simple device, which when placed on the sample forces a truncated double cone (*see 3.1.1*) against the coating by means of a load of 500 g. The length of the mark is measured with a microscope after removal of the instrument. It should be regarded as a "practical" instrument.

Reference should be made to two simple test devices[30, 31], in which the position of the indenting tool is indicated by the liquid meniscus in a capillary tube attached to a small fluid tank. In this way a magnification of 2000 : 1 is attained, permitting detection of movements of fractions of a micron. None of these instruments nor the following is intended for use with coatings.

Böklen[32, 33] takes into account that compression of the sample support may falsify the indentation values; in his Testorgraf the movement of the indentor is measured in relation to the sample surface rather than in relation to the support; the principle may be useful in connection with coatings on compressible substrate.

3.1.3 Additional literature

The principle of the Brinell hardness test, *i.e.*, indentation and subsequent microscopical measurement, was applied to coatings in 1932 in the CTR method[34] which used small loads and a diamond pyramid as the indenting tool. Okhrimenko and Kolin[35] describe a similar procedure performed with the Russian apparatus PMT-3 and compare it with pendulum results. Kuntze[19] recommended using a cone with a flare angle of 136°.

Maxwell[36] investigated the influence of temperature, load and loading rate on the hardness of plastics and stated that the differences in behaviour of different plastics, particularly in comparison with metals are due to their relaxation behaviour. Maxwell[36] as well as Bradley[37] employs the Tukon hardness tester with the Knoop diamond. Bradley deals with the dependence on temperature of the hardness of epoxy resins and in particular the determination of the softening temperature by hardness measurements.

Augustsson and Danielsson[25] applied the Wallace instrument with the Vickers pyramid to stoving enamels and compared with a hand test, the pendulum test and the pencil test. Haldenwanger[38] has given a survey of all the indentation methods for plastics and the relation between them; Kruse[39] and Nitsche[40] discuss fundamental difficulties in hardness testing on plastics.

3.2 Damping methods

3.2.1 General

Damping methods work on the common principle that a suitable tool with a known content of kinetic energy impinges on the surface of the sample, deforms this and thereby loses a certain amount of its energy; the loss of energy is somehow converted to a softness or hardness figure. These methods differ from most others in that hardness is judged from the effect of the sample on the tool instead of the reverse. Since the loss of kinetic energy can easily be observed with the naked eye as big movements of some marked point on the tool (or an attachment to it, *e.g.*, a pointer) the devices are extremely simple and very suitable for practical application. Unfortunately, the ease of measurement is accompanied by difficulties in interpretation as well as in translation into practical terms, and the figures obtained may lead to large errors if accepted straight away. Nevertheless such devices have become very popular and useful as control instruments because the figures often run roughly parallel to some practical hardness

concept, and above all because variations of damping properties indicate that the mechanical properties of a material have not been kept constant.

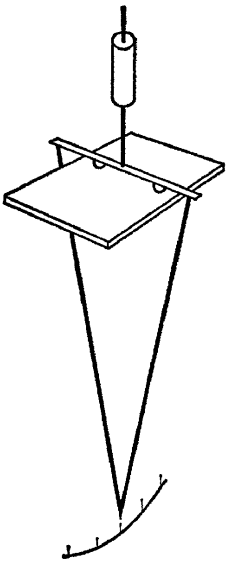

Figure 9. Schematic diagram of a pendulum hardness tester. (After König[42])

For a pendulum in its usual form, the tool comprises two steel balls resting on the horizontal sample surface; a connecting bar forms the upper side of a vertical frame which encircles the sample (*Figure 9*). As the centre of gravity of the frame is below the balls the set-up is a pendulum, which, when swinging, gives the balls a reciprocating rolling movement on the coating; at the same time the film is deformed by the weight of the set-up, the loss of energy manifesting itself in a decreasing amplitude of swing. In case of rockers two connected parallel wheels roll forwards and backwards on the coating because the centre of gravity is placed off the wheels axis; again the rate of decrease of amplitude is measured, usually as the time or the number of swings between two fixed amplitudes.

Passing reference should be made to the rebound test which is used more for plastics than for coatings; an instrument of this kind was described by Haken[41].

The theoretical limitations of damping tests have been dealt with earlier (*2.3.2*) but more practical difficulties also arise mostly due to external conditions.

The results obtained depend of course on the shape and size of the indenting body, on the weight of the instrument, on air damping and on oscillation frequency[42–45]. When, as is usual, the rate of decrease of amplitude is recorded instead of energy consumption, the distance between the test surface and the centre of gravity also becomes important. Such factors must be standardized in connection with the particular types of instruments. Measurements must be performed in a draught-free place, this being more important with rockers than with pendulums.

With some materials a pronounced increase of "hardness" with decreasing layer thickness is present and with others no such dependence can be detected; this is true even if the mechanical properties of the film substance do not vary with the layer thickness. The effect is a reflection of differences in relaxation behaviour between different materials; it stresses the difficulties with interpretation and makes a comparison of two otherwise unknown coatings very difficult, for what is measured is some property of the coated object and not of the film substance alone.

Taking this into account it is no wonder that a good correlation is found between different instruments with some materials[11], while it breaks down completely with others.

With some soft coatings the tool creates a deep groove in the coating whereby high hardness is simulated. In general the measurements are sensitive to conditions of contact between tool and coating, *i.e.*, to surface roughness of tool and coating, contaminations and tackiness.

3.2.2 Apparatus

Pendulums.—The various pendulums that are in use are very similar and differ mainly in size of balls, weight and time of swing. The Persoz pendulum described, *e.g.*, by Bermane[46] is heavier and has bigger balls than the König pendulum[42] but usually gives similar results[11]. The König instrument is more convenient to handle as it is supplied with mechanisms for placing the pendulum on the test surface and for the release of it with a defined amplitude of swing. It has been standardized in Germany (DIN 53157)[47] and adopted by the European Harmonisation Commission[48a] as a future European standard. The Swedish SOAB pendulum and the standardized Russian pendulum (GOST 5233-50)[49] are similar devices; in the last one the sample is surrounded by a water-jacket to permit measurements at various temperatures. Some pendulums can be procured with photoelectric counters to afford automatic measurement and recording.

Rockers.—With the best known instrument, the Sward rocker[16], which is very much used in the U.S.A., one counts the number of swings between two fixed amplitudes indicated by two libellas attached to the wheels, a calibration being undertaken on a clean glass plate. Many papers describe its use and the difficulties encountered. Moore[50] and Baker, Elleman and McKelvie[51] report on subjective differences between observers in such matters as reading the initial and final points of the vibrations; according to Monk[52, 53] such variations are largely eliminated by the use of magnetic release and photoelectric counting of the number of swings. The most detailed investigation on the error sources of the Sward rocker has been carried out by the Paint Production Club of Los Angeles and reported upon by Bosco[54]. Influences of temperature on libellas, damping by air friction and shape of rings (wheels) are dealt with and it is proposed to use plastic plates for calibration instead of glass. Similarly Raaschou Nielsen[43] reports on differences between individual instruments due to different dimensions and stresses the necessity of calibration.

3.2.3 Additional literature

The historical development of "damping" measurements is dealt with

by Gardner[16] and Wilborn[17]. Heyne[55] compares results obtained with a German rocker[56] and the Persoz pendulum, concurrently investigating the effect of temperature, inclination of samples *etc.* The same rocker is compared to scratch hardness testers and Pfund indentation tester[16] in a paper by Zeidler and Roesler[56]. Crovetto[57, 58] draws attention to the influence of temperature and humidity on damping measurements. A mathematical treatment of testing with a pendulum can be found in a Japanese paper[59].

3.3 Scratch methods

3.3.1 General

The common feature of the scratch tests is that a loaded tool is drawn across the test surface, the effect of this being evaluated by a coarse or more refined visual observation.

Such a simulation of practical conditions appeals to most technologists and is obviously the best choice in a number of cases, yet the idealization of the conditions for making the scratch test may not at all concern the practical factors of influence; thus the results may be erroneous or misleading. The search for relevant instruments has resulted in numerous forms, so that this group of tests is not nearly as homogeneous as the two preceding ones. They differ not only with regard to instrumental details such as load, shape and velocity of tool, but also with regard to the effect on the coating and the evaluation of this effect. The methods of evaluation can be divided in three with definitions of hardness as (*i*) the necessary force on the tool to penetrate to the substrate, (*ii*) the force that creates a scratch of certain dimensions or just a visible scratch without baring of the substrate and (*iii*) the necessary strength properties of the tool material to make possible the formation of a visible scratch. This latter is the equivalent of the Moh hardness scale used for minerals.

The first case, which is the most common one, involves such large stresses on the film, that usual deformation theory fails and, furthermore, breaks of different kinds may arise. Also, because of the close proximity of the tool to the substrate, adhesion becomes a factor of influence, as well as the mechanical properties of the substrate itself. In short the results tell what happens to a coated object under the conditions of the test and any further interpretation is left to the experience of the experimenter.

In the second and third cases, the influence of substrate and adhesion is less or even vanishing, but the necessary determination of the dimensions or the visibility of the often ill-defined scratch is difficult and inaccurate.

In general scratch tests show poor reproducibility; variations of 30–40 per cent are usual although better results are obtained in special cases[11, 60]. One reason for this is the sensitivity of these tests to the surface conditions, *e.g.*, contamination with oil or silicones often leads to drastic improvements of scratch resistance. Other causes are due to difficulties in obtaining a perfect, even movement of the tool and abrasion of the tool tip.

With plastics, microscopic measurement of scratch dimensions is easier than with coatings because the size can be bigger, yet the results are not too good. Bernhardt[61] noted the pronounced influence of velocity on the results when using a sapphire cone with a flare angle of 120°. A scratch method for plastics (according to Bierbaum) is standardized in the U.S.A.[62].

3.3.2 Apparatus and methods

The more typical forms are described in summarizing books[16, 17]. The DEF apparatus and method[63] has been widely used. With it the load is kept constant during the scratching process just as with the Clemen-Keyl scratch tester[17], much used in Germany. With both, the load necessary for through scratching is determined. However, while the first has a ball-shaped tool, the second employs a kind of knife. Toeldte[64], Niesen[65] and Siim[66] have tried to detect through scratching by means of electrical contact between tool and substrate, while Sheppard and Schmitt[67] applied microscopical observation to the same end.

Instead of operation under constant load Kempf[68], Hoffmann[69] and Shikker[70] consider that better and faster judgment is possible when the load is continuously increased with the scratch distance; the accompanying mechanical problem is solved in a very elegant way in the Dantuma tester[71] and further in the Rondeau tester[72]. Wear of the tool is an important factor, as commented on by Dantinne[73]. All the papers mentioned deal more or less with the difficulties and error sources of scratch hardness testing.

The pencil hardness test, which is an adaption of the third principle above, is so simple that it could also be regarded as a hand test (*see* **4.6**). The tool substances chosen are pencil leads, the hardness designations of which characterize their strength properties. With it there are many influencing factors[74], such as the pressure and velocity used, the sharpening of the pencils, the angle of incidence during the scratching, the brand of the pencils and uncertainty in connection with the lead manufacture. Useful information is also given by Gardner[16]. In a Dutch method, which has been adopted as European standard[48b], the pressure is fixed and a reproducible start of the scratching is obtained by means of a razor blade lying on the coating; the pencil movement commences on the blade and proceeds on the coating.

Considering that most coatings have a hardness which lies between 2B and 4H and that there is an uncertainty in the determination of at least one degree, it must be accepted that the pencil hardness can only give a coarse division into about six groups. In the careful investigation by Gusman[15], Knoop hardness and pencil hardness on 78 baked finishes show good correlation†, with deviations of 1–1½ pencil units from strict relationship. Hiron, Rudd and Zonsveld[75] compared pencil hardness with other hardness tests.

With the simple pencil-like instrument of Weinmann[76, 77] the hardness is determined as the necessary force on a ball-ended needle to create a visible scratch.

3.4 Abrasion tests

3.4.1 General

With abrasion tests the grains of a grainy material are forced against the sample surface causing deformation and breaks of the coating surface either by a scratching process or by impact; hardness is judged as high if little coating material is removed, and lower if more of it is removed. Thus many

† Knoop hardness is approximately equal to 0·18 times the squared pencil number, when pencils from 6B to 6H are numbered 1 to 14 (author's remark).

scratching or impacting tools are used concurrently and the effect is a cumulative one, which is usually determined either by the loss of weight or by the extent of action needed to reveal the substrate. As with the scratch tests such properties as mechanical strength, extensibility, and adhesion to the substrate are important factors, but furthermore clogging of tool and sample surfaces takes place to a degree determined by the stickiness of the abraded material; this is often amplified by temperature rise under the intense mechanical action. The film surface may even melt superficially.

As with all other hardness tests a characteristic of the film substance can be obtained only if the groove or scratch created by each individual tool is small in width and depth compared to layer thickness, *i.e.*, if the coating is abraded gradually, uniformly, and superficially. The higher the pressure on each particle, or in case of impact its kinetic energy, and the bigger and blunter the grains, the more will the forces and effects penetrate to possibly weak interfaces and to the substrate, and the less does the test usually agree with the term hardness test. Thus, for example, scrubbing with fine sand could meet the requirements, while blasting with steel balls stressed interfacial effects to such a degree that it is more appropriate to speak of an impact test.

Although good reproducibility is obtained with certain combinations of apparatus and coatings the general opinion is that abrasion methods are very imprecise and inaccurate. In any event, very careful standardization of test conditions is necessary, whilst the interpretation of results is difficult and should be supported by experimental verification of a supposed agreement between testing and practice.

3.4.2 Apparatus

The abrading grains may be in a fixed relative position as on sandpaper or detached as in a particle jet.

The first arrangement is used in the Taber abraser in which a wheel of a rubber compound with imbedded carborundum particles rolls, and at the same time slides, on the test surface under a given pressure. It has been standardized in the U.S.A.[78] and has also been used in Scandinavia for the testing of floor varnishes, and results have been very reproducible, but not always in accordance with practice[79, 80]. This is particularly evident with comparisons between varnishes of widely different compositions. A paper by Hill and Cook[81] discloses similar troubles.

In the apparatus of Weinmann[82] continually renewed emery paper is used for abrasion of a superficial part of the film in an effort to avoid clogging; reproducibility is good but quantitative differences between the hardest and the softest coatings are surprisingly small in comparison with practical experience. This is probably due to the fact that the practical application does not normally meet abrasion by such a hard material as emery.

For such reasons Uetz and Wellinger[83] have developed a blast apparatus in which materials of different hardness in grain form have been tested as jet material. However, on tests carried out in Stuttgart with this device too much dirt remained adherent to the coating particularly with the softer types of coatings, impairing reproducibility. More typical examples of the second arrangement—detached particles—are the falling sand method

(ASTM D 968-51)[84] and the air blast method with silicon carbide grain (ASTM D 658-44)[85]. To obtain increased reproducibility, which is generally poor with both methods, the first method was modified by Boller[86] and the last by Roberts[87, 88].

3.4.3 Additional literature

A survey of abrasion methods was given by Haken[89] for coatings and by Boor[90] for plastics. Haug[91] compared results of the Weinmann method and the falling sand method applied to coatings. Testing and practical results were compared for rubber by Prat[92].

4. HAND TESTS OF HARDNESS

4.1 General remarks

Hand tests are here defined as tests that do not require any special tools, *i.e.*, either no tools at all as with a nail scratch test or articles from every-day life only—a coin, a pencil *etc.* Long before scientific paint research had begun these tests were already in use and they are still considered to be indispensable.

This is understandable. From the definition given it follows that they are simple, do not require scientific consideration or design of complicated devices nor large expenditure.

The aim of this investigation was not so much to give a complicated theoretical interpretation nor to criticize the hand tests, but to apply some generally known facts of rheology to the existing procedures. This could help those who apply these tests to acquire a better understanding of what they are doing, and where they can apply the different tests.

The application of the tests concerns the producer as well as the user of paints. For the producer a better understanding of the tests may be helpful when considering improvements of his products. The user may be better informed about the application possibilities. The practical hardness hand tests dealt with here have been assembled by an inquiry in several European countries. They are thought to be representative for the trade. Each type of test will be dealt with separately in more detail.

The rheological concepts which are used here may be found in Chapter 2. It may be appropriate to realize that conceptions such as soft and hard are derived from the human body, several parts of which serve as a standard. This is not as absurd as it may seem at first, because most of these parts have a macromolecular structure too. Thus *soft* means comparable to the fingertips, *hardness* is the quality of the nails, *very hard* is like the teeth, and *very soft* like the tongue or the lips.

This connection has not only a psycho-linguistic meaning but is also of technical importance. Firstly, much of the testing is done in fact by means of parts of the human body: fingers, nails, even teeth in some cases, and secondly, the painted article when handled has often to stand the mechanical influences of some of these parts themselves and/or of these parts covered with some other macromolecular composition, *e.g.*, trousers, gloves and shoes made from wool or cotton or leather.

4.2 Thumb tests

There are several ways of performing thumb tests.

4.2.1 The thumb pressure test

Method.—A vertical pressure is exerted on the film surface with the ball of the thumb, and the extent to which a mark is left in the film is noted.

The action itself is one of pressure of a relatively low value per unit of surface. Thus, it seems that the test is meant for comparatively soft paint surfaces (*see* **4.1**) and in fact its chief use seems to be as control of through-drying of air-drying films.

The result of the action of the thumb pressing vertically is possibly a lasting indentation. It should be noted that the time of duration of the indentation is not given, nor the time after which the mark's presence is observed. This might be completed in a standardized version of the test.

As to the time of pressure, let us assume that the investigator tries to obtain some indentation, then he will tend to press till he feels some change. To obtain this with soft films, he will only have to press for a short time. With harder films he will have to press longer. Harder films will therefore be subjected to a higher rise in temperature, the thumb being warmer than the film. In so far as a higher temperature lowers hardness, the effect is a certain levelling of results. For practical reasons, the maximum time of pressure may be taken as about half a minute.

The phenomena that occur with the thumb test may show a great variety, yet in each case they can often be interpreted by means of a rheological model such as the one given in Chapter 2 (*Figure 1*). The utility of such considerations is that the paint formulator will be able to associate the elements of the theoretical model with the properties of the components of his formula and get a unified picture of the deformation processes facilitating formulation.

When the thumb is pressed against a homogeneous film irregularities of the pressing surface, in particular the peculiar pattern of the finger-print will cause local variations in pressure. The film substance will be redistributed by movements from zones with high pressure to zones with low pressure causing the pattern to show up in the mark made. This only involves movements over small distances which can take place with comparative ease, while removal of material from the entire pressure area involves displacement over long distances and only takes place to a minor extent.

Oxidizing films are often composite in the sense that they have a well-dried hard top layer, almost in the glassy state, resting on a layer consisting of a rubbery gel. In this case the pressure pattern is transmitted by the top layer and causes flow sideways in the second layer; the top layer will then adapt itself to the resulting pattern in the second layer without any horizontal displacements by slight vertical movements of elastic character and thus present a mark.

The viscosity of the second layer, which is lower than with the top layer, as well as the thickness, will play an important part in the speed of the deformation, and will therefore influence the relation between mark depth and time of pressure.

4.2.2 The pressing and turning thumb test

Method.—The ball of the thumb is pressed against the film surface and rotated through an angle of 90° or more about a vertical axis. The extent to which a mark is left is noted and taken as a measure of softness.

As with the test in *4.2.1* the principle use of this test seems to be for the control of through-drying of air-drying films. It can also be performed with

the so-called "Artificial Thumb",†[93, 94] which consists of a loaded plunger, tipped with rubber and covered with a piece of cloth. The plunger is automatically lowered and rotates through 270° while being pressed onto the painted panel. The fixation of such variables as dimensions of the "thumb", pressure, angle of rotation and time conveys an increased reproducibility, which is desirable especially for specifications. The criterion of this test, which applies to metal panels coated with the paint is removal of the film.

During testing similar phenomena will occur as with the thumb test described in *4.2.1.* If the film is hard throughout, then the additional rotation will have little effect because of the limited friction between thumb and film; but in the case mentioned of a film with a hard top layer resting on a soft gel the movement of the top layer is eased and the friction causes it to rotate. The part under the pressing body will turn as an entity, but at the circumference and outside of it folds will be seen more or less like tangents to the outline. No doubt the film is strained here resulting in an enlargement of its area. The folds follow the direction of the tensile strain, which is roughly at an angle of 45° to the outline. Ultimately the strain may result in rupture.

According to particular needs different scales can be used to evaluate the extent to which a mark is left. The simplest kind only differentiates between two conditions such as a visible mark and no mark at all or between rupture of the film and no rupture (*cf.* **2.3**); as rupture is a kind of visible mark the first criterion is the most severe. The fact that both criteria are used reflects the different interpretations that can be put upon the words "deformation" and "damage" used in the hardness definitions (*cf.* **1.1**).

4.3 Nail tests

Four nail tests will be mentioned here: indenting, shearing and grazing action by the thumb-nail, and grazing of a different kind by the four smaller nails.

The results obtained in these tests, particularly in the first two cases, depend on the condition of the nail: a newly washed nail is relatively soft and using a short nail constitutes a more severe test than a long one.

4.3.1 The indenting thumb-nail test

Method.—A vertical pressure is exerted for a certain time on the film surface with the front edge of the vertical thumb-nail. The size of the mark created is taken as a measure of softness.

This test differs from the thumb test in that here one dimension of the indenting object is comparable to the thickness of the paint film. Therefore it comes closer to a straightforward indentation test and less of the paint film's material needs to be transported to obtain a certain indentation value, compared with what happens in the thumb test. Hence, the squeezing out of the film substance is more pronounced here than with the thumb test and the influence of time will be more apparent. Within the usual length of time the indentation increases, provided that the force persists. This is one of the secrets of "hard nails"—to hold on, even when it hurts.

† Strictly speaking this is not a hand test, but it is mentioned here because it is a close imitation of the human thumb test.

When the indenting nail is approaching the substrate, the resistance met by it will increase, partly because the film substance is forced under the nail's pressure in a viscous flow through a narrower passage than before, and partly because the elastic deformation of the remaining film part under the nail is more difficult the thinner this part is.

For these reasons, a thinner coat appears to be harder. Thus, even in such simple tests as nail tests, the thickness of the paint coat should be specified (even if the influence of thickness on through-drying can be disregarded).

In the above it has been assumed that the film adheres to its substrate; but if the adhesive forces are yielding, the lower layers of the film are very easily pushed aside. The indentation movement will meet with less resistance and the film may be judged to be softer if the lack of adhesion is not recognized. Similarly, if rupture takes place under the nail because the substance is not sufficiently ductile the indentation will proceed more easily.

Such effects are more common with the nail test than with the thumb test because of the much higher pressure per unit area of the indenting tool.

4.3.2 The shearing thumb-nail test

Method.—The thumb-nail is held vertically against the film surface. An attempt is made to remove the film by drawing the thumb-nail at right angles to its own plane, exerting a strong downward pressure to the film. The film is considered the harder the lesser the amount of film substance that is removed.

If any substance is removed, break or at least destruction of cohesion must occur; thus this test is not immediately comparable to the indenting thumb-nail test (*4.3.1*). Yet no material can be removed unless the nail penetrates into the film and the test can therefore be regarded as a dynamic indentation test, while the other one is static (*cf. 2.3.4*). If adhesion is not sufficient to withstand the high stresses under the nail, the film is easily torn and peeled off the substrate; accordingly the test is often used to evaluate adhesion rather than hardness.

4.3.3 The grazing thumb-nail test

Method.—The thumb-nail is held with its face downwards and towards the operator at an angle of 45° to the film surface and moved fast and lightly over the surface towards the operator. It is noted whether any mark is left on the surface.

This test might be called "mar proofness test No. 1" as it, as well as the next test, is connected to the somewhat vague notion of mar resistance.

Marring is a damage to the visual appearance of a paint surface without any visible indentation of the surface. Since apparently only the very surface of the paint is involved it is somewhat doubtful whether the evaluated property has anything to do with the deformation properties of the entire film substance, *i.e.*, with its hardness, or whether it is due to an abnormal composition and behaviour of a thin surface layer. Yet it is felt that there is no justification for leaving these tests out.

Mar damage may be damage of an extensive nature as from rubbing a piece of cloth or leather against a painted bench or floor, or from a branch of a bush brushing against the paint on a car.

The action of the thumb leaves a track several millimetres wide, if any. The action seems partly one of friction, partly one of pressure, compared with the next test, with emphasis on the last. The film may show rupture signs at right angles to the movement. All parts of the track are subjected to a successive short-time indentation in a direction somewhat deviating from perpendicular in accordance with the movement made. The test is similar to the next one, in that it is a friction test. High viscosity, low thermoplasticity and high elongation at break will give favourable performance with this test.

4.3.4 The grazing smaller nails test

Method.—A grazing reciprocating motion is made on the film surface with the front edge of the index finger-nail, possibly with the edges of the four non-thumb nails, moving the hand parallel to the plane of the nail(s). Any marks left on the surface are noted.

Referring to *4.4.3* this test may be called "mar proofness test No. 2".

The friction between the nail(s) and the paint implies a substantial increase of temperature in the surface of the film, which is greater the faster the movement and if the film substance is thermoplastic its surface will become soft and maybe even melt. Thus a mark is easily created.

Films showing the same resistance to indentation at room temperature may have very different resistances towards the grazing nail, because of differences in thermoplasticity. However, differences in composition of surface and bulk film are important too, as shown by the fact that the addition of certain substances, *e.g.*, waxes or silicones, is often followed by a marked improvement in mar resistance, leaving all other kinds of hardness unchanged.

In view of the practical importance of mar resistance some workers have used an artificial nail (ivory, plastic) with mechanically controlled load and velocity.

4.4 Knife tests

With the following tests the tool is the curved part of a knife edge.

4.4.1 The scraping knife

Method.—The knife blade is held in a vertical position, forcing its edge against the film under great pressure and it is moved rapidly at right angles to the plane of the knife blade; the degree of difficulty of removal of the film is noted.

The scraping knife test closely resembles the shearing thumb-nail test (*4.3.2*). The difference lies in the use of a knife in the former. The indenting surface is smaller and the force of the knife-holding hand will exceed a thumbs' force. Therefore the force per unit of surface will be much larger and the elongation at break and other ultimate properties will play an important part and so will adhesion. In fact the test is more often regarded as an adhesion test than as a hardness test. As the knife is moved at right angles to the plane of the blade the force concentration is not very high

during this phase of the test; the knife scrapes but does not cut. The result is often markedly dependent on the velocity of the movement.

4.4.2 The peeling knife

Method.—The knife blade is held at an angle of 45° to the surface, pressed and moved at right angles to the edge, attempting to peel off a strip of the film. The degree of difficulty of removal of the film is noted.

The considerations described with the previous test also apply here. However, with the peeling knife test the edge leads the movement and creates a very high concentration of forces parallel to the surface. The force of rupture will be reached comparatively easily which results in a cutting action. This cutting is as well directed downwards and the knife-edge will more or less follow the surface of the substrate, which must be hard. Accordingly the properties of the film at the interface or close to it are very important and this test is thus even more of an adhesion test than the preceding one. Yet it is also a hardness test because the difficulty in removing the film is to a large extent governed by the elasticity, plasticity and strength of the film. It is left to the experimenter to apply his skill to the interpretation of the test in each case. This also applies to the interpretation of the detailed appearance of the scratch made.

4.5 Coin tests

4.5.1 The scraping coin test

Method.—A coin is held in a vertical position under great pressure against the film and moved at right angles to the plane of the coin. The film is the harder the less the film is affected.

This test is similar to the shearing nail test (*4.3.2*) and the scraping knife test (*4.4.1*), but it is less severe than the latter because of the more blunt edge of the coin. As damage, particularly with metal objects not sharpened on purpose, may often occur in practice, this test is not out of place.

4.5.2 The rolling coin test

Method.—A milled coin is rolled along the surface of the film under pressure. The hardness is evaluated according to the size of the impression made. In England the test is sometimes called the "half crown" test.

4.6 The pencil test

Method.—The point of the lead of the pencil is sandpapered so as to make a sharp-edged, plane surface at right angles to the direction of the pencil. The pencil is held in a slanting position at about 45°, pressed against the film surface and pushed in the direction indicated by the pencil point. The "hardness" of a film is taken as the hardness value of the hardest pencil which does not leave any mark, *i.e.*, sign of deformation or abrasion on the film surface.

The pencil differs markedly from other testing devices because abrasion of the tool plays an important part. Pencils of different hardness designations are of different mechanical strength and thus the forces, that can be transferred to the film at a certain pressure and speed, are limited; no force exceeding the strength of the lead can be applied to the film. The selection

of the right pencil is therefore a determination of the strength of the film surface.

The result cannot be considered absolute, since pencils with the same hardness designation, but manufactured by different factories, may give different results. The kind of effect on the film which will range from temporary or lasting deformation to rupture, is determined by such properties as viscoelasticity, yield value and rupture strength. Further information about this test was given in *3.3.2.*

4.7 Impact tests

4.7.1 The impact rod test

Method.—The protective coating to be tested is applied to two rigid iron rods or tubes and after drying they are struck against each other. Lack of visible deformation of the film is taken as an indication of "hardness".

This test which is not used very often is considered to be a very severe one. It is severe because, apart from other considerations, the meeting surface of the two cylinders is geometrically one point only and therefore the force per unit of surface is rather large, even if elastic deformation enlarges this point to a saddle-shaped surface.

The film is pressed by the two approaching iron rod substrates and elastic and plastic deformation, or even rupture in the film or in the film-substrate interface (peeling), may result. The friction and the adhesion between the film faces are important and a bit of wax or mineral oil can work miracles. Thin coatings are harder than thick coatings with this test.

4.7.2 The nut fall test

Method.—A number of medium-size steel nuts are dropped onto a painted panel, orientated at 45° with the horizontal plane. The area of loosened film from substrate or primer is measured or estimated.

The test is very complex. Generally a low indentation hardness value is favourable, and so are good adhesion and good performance with a bending test.

4.8 Imprint resistance

Method.—A cheese cloth is placed on the painted surface and covered with a felt layer. A weight is placed on the felt, which evens out variations of load per unit area. The degree of permanent impression after a certain time under a certain load is less, the harder the film.

A very similar method using metallic wire gauge and rubber disc instead of cloth and felt has been adopted as a European standard[48c] for the determination of through-drying time.

Both procedures are reminiscent of the thumb test (*4.2.1*) and most of the remarks and explanations given there apply to them.

5. STANDARDS AND COMMONLY USED METHODS

As a concluding chapter to the present publication, tables of standardized and other commonly used hardness testing methods have been compiled on the following pages. The greater part of the methods listed has been based on information submitted by members of the eleven countries represented in the Organic Coatings Section of the International Union of Pure and Applied Chemistry. Additional information was obtained by the Danish Standards Association through contacts with the standardizing organizations of eight countries, who are not represented in the Organic Coatings Section, but who have an extensive production of paints and varnishes.

A first draft of the compiled list was forwarded to all contributors for comments and supplementing, but even the revised list as it appears bears the impression of heterogeneity, and there can be no doubt that it is incomplete. It is felt, nonetheless, that the present list will be a helpful reference for anyone concerned with the practical testing of paints and varnishes.

The methods have been listed in the following four tables: indentation hardness tests, damping hardness tests, scratch hardness tests and abrasion tests. In each table the methods have been divided into internationally standardized methods, standardized methods and non-standardized methods. Standardized methods mean those that have been adopted for use within a single country by some important standardizing body irrespective of its status, governmental or otherwise. The standardization is regarded as international if corresponding bodies in two or more countries have agreed upon a common text. With the adoption by the Harmonisation Commission of the Comité Européen in 1946 of the methods for determining scratch hardness with pencils (CHM 05–64) and damping hardness with the König pendulum (CHM 04–64) these two methods are certain to become standardized in several member countries of the Comité Européen in the near future. Therefore they have been listed as internationally standardized methods. Furthermore, it should be mentioned that the International Standardization Organisation (ISO) has extended its work within the field of protective coatings by setting up under the ISO/TC 35 (raw materials for paints, varnishes and similar products) a sub-committee (SC 9), the purpose of which it to work out draft recommendations for test methods for paint and varnishes. Under the heading non-standardized methods have been listed commonly used tests that have not been standardized within the particular country under which they are mentioned.

Table 1. Indentation hardness tests

Standardized methods

Country	*Title*	*Number*	*Authority*	*Comments*
Germany	Eindruckversuch an Anstrichen nach Buchholz	53 153	DIN	Widely used for hard coatings
U.S.A.	Indentation hardness of organic coatings (*a*) Knoop indentation hardness (*b*) Pfund indentation hardness	1474–62T	ASTM	

Non-standardized methods

Country	*Apparatus used*	*Comments*
Denmark	Wallace indentation tester	Mainly used for research and development, not for control tests
Germany	Vught indentation tester	Ditto
Great Britain	Wallace indentation tester	Ditto
Nether-lands	Vught indentation tester	Ditto
	T.N.O. indentation tester	Ditto
	Buchholz apparatus	According to DIN 53 153
Switzer-land	Apparatus using a Vickers pyramid as indentor	Mainly used for research and development, not for control tests
Sweden	Wallace indentation tester	Ditto
U.S.S.R.	Apparatus PMT-3	Uses a diamond pyramid similar to the Vickers pyramid as an indentor

Table 2. Damping hardness tests

Internationally standardized method

Title	*Number*	*Authority*	*Comments*
Pendulum hardness determination	CHM 04–64	Com. Eur.	Based on DIN 53157

Table 2—continued

Standardized methods

Country	*Title*	*Number*	*Authority*	*Comments*
Canada	Sward hardness	1–GP–71 no. 104·1	CGSB	
Czecho-slovakia	Measurement of the hardness of paint films with the pendulum apparatus	673076	ČSN	
Denmark	Determination of damping hardness	D 46/1	FDLFI	= CHM 04–64
France	Essai de dureté pendulaire des peintures	30 016	AFNOR-NTF	Persoz pendulum
Germany	Schwingungsversuch mit dem Pendelgerät (nach König) zur Beurteilung der Härte von Anstrichen	53 157 (Entwurf)	DIN	
Italy	Hardness determination with the rocker	f-7	UNICHIM	Sward rocker
Sweden	Determination of hardness with pendulum	18 41 86 (Tentative)	SIS	= DIN 53157
U.S.S.R.	Determination of the hardness of coating films with the pendulum apparatus	5233–50	GOST	

Non-standardized methods

Country	*Apparatus used*	*Comments*
Belgium	Persoz pendulum	According to AFNOR-NTF 30 016
Denmark	Sward rocker	Not as widely used as the König pendulum
Germany	Schaukelhärteprüfer	Rocker, not as widely used as the König pendulum
Great Britain	Sward rocker	Most commonly used apparatus
Nether-lands	Persoz pendulum König pendulum Sward rocker	According to AFNOR-NFT 30 016 According to DIN 53 157
Switzer-land	König pendulum Persoz pendulum Sward rocker	According to DIN 53 157, preferred apparatus According to AFNOR-NTF 30 016
Sweden	SOAB pendulum	
U.S.A.	Sward rocker	
U.S.S.R.	Pendulum	Adapted for the determination of damping hardness between 20° and 200°C

Table 3. Scratch hardness tests

Internationally standardized methods

Title	*Number*	*Authority*	*Comments*
Pencil hardness determination	CHM 05–64	Com. Eur.	Based on VVVR 19
Hardness (Pencil method)	Article 22	ORE	

Standardized methods

Country	*Title*	*Number*	*Authority*	*Comments*
Canada	Scratch hardness	1-GP-71 no. 116·2	CGSB	= DEF 1053 no. 14
Czecho-slovakia	Measurement of the surface hardness of paint films with pencils	673075	ČSN	
Denmark	Pencil hardness determination	D 46/2	FDLFI	= CHM 05–64
Great Britain	Scratch resistance	1053 no. 14	DEF	Scratching with a 1 mm ball
Nether-lands	Pencil hardness	19	VVVR	
Portugal	Scratch resistance	235	NP	= DEF 1053 no. 14
Sweden	Determination of scratch resistance with pencils	18 41 87 (Tentative)	SIS	= CHM 05–64
U.S.A.	Adhesion (Scratch test)	FTMS 6306	GSA	Apparatus used: Hoffman scratch hardness tester

Non-standardized methods

Country	*Apparatus used*	*Comments*
Belgium	Clemen apparatus	
Germany	Pencils	Method from 1929, which prescribes the use of a lead with round end
Great Britain	Pencils	
Nether-lands	DEF 1053, no. 14 apparatus Dantuma apparatus	
Switzer-land	Clemen apparatus Pencils	Several methods used
U.S.A.	Pencils Mechanical scratch testers	Widely used 16 different versions listed in Gardner[16]

Table 4. Abrasion tests

Standardized methods

Country	*Title*	*Number*	*Authority*	*Comments*
Canada	Abrasion resistance	1-GP-71 no. 104·1	CGSB	Uses falling carborundum
Sweden	Determination of dry abrasion	18 41 65 (Tentative)	SIS	Uses falling carborundum
U.S.A.	Abrasion resistance (air blast)	D 658–44	ASTM	Carborundum
	Abrasion resistance (falling sand)	D 968–51	ASTM	Ottawa sand
	Abrasion resistance (falling sand)	FTMS 6191	GSA	= ASTM D 968
	Abrasion resistance (Taber abraser)	FTMS 6192	GSA	
U.S.S.R.	Determination of abrasion resistance of organic coatings	10086–39 method 23	OST	Uses falling sand
	Determination of abrasion resistance of shellac varnish	7573–55 par. 13	GOST	Uses falling sand

Non-standardized methods

Country	*Apparatus used*	*Comments*
Denmark	Taber abraser	Used for the investigation of floor varnishes
Germany	Abriebprüfgerät nach Stock und Keyl	Uses standardized sand
	Abriebprüfgerät nach Bosch–Weinmann	Uses emery paper
Sweden	Taber abraser	Used for the investigation of floor varnishes
Switzerland	Falling sand apparatus	
	Taber abraser	

Abbreviations used

AFNOR	Association Française de Normalisation
ASTM	American Society for Testing Materials
CGSB	Canadian Government Specifications Board
ČSN	Czechoslovak National Standard
Com. Eur.	Comité Européen des Associations de Fabricants de Peintures et d'Encres d'Imprimerie
CHM	Commission pour l'Harmonisation des Méthodes d'Essais des Peintures et Vernis (set up by Com. Eur.)
DEF	Defence Specifications (British)
DIN	Deutsche Industrienormen
FDLFI	Danish Varnish and Paint Manufacturers Association
FTMS	Federal Test Method Standard no. 141 (U.S.A.)
GOST	State Standard (U.S.S.R.)
GSA	General Services Administration (U.S.A.)
NP	Norma Portuguesa
ORE	Office for Research and Experiments of the International Union of Railways
OST	All-Union Standard (U.S.S.R.)
SIS	Swedish Industrial Standard
UNICHIM	Group for Chemical Standardization (Italy)
VVVR	Paint Research Association (Netherlands)

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