RP333

A NEW TEST FOR PREDICTING THE DURABILITY OF VARNISHES

(THE PHOTOCHEMICAL EMBRITTLING TEST)

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ABSTRACT

The test described in this paper for evaluating varnishes consists in two operations. A varnish film is first exposed to an intense source of light for a definite period of time, after which it is bent double at a prescribed temperature over a rod of fixed diameter. The data presented show that the more durable the varnish, the longer it may be exposed to the light before it will crack on bending.

This text possesses a number of advantages over those now in use for this purpose, due to the simplicity of preparing the samples and making the test, and the speed with which results can be obtained.

CONTENTS

I. INTRODUCTION

In recent years various investigators[1] have devoted considerable time to developing methods for predicting the durability of varnishes.

The two tests used for this purpose at the present time are the kauri reduction test[2] and the accelerated weathering cycle.[3] The former has been found to give fairly satisfactory results when comparing the same type of varnishes, but is not suitable for the comparison, for instance, of a varnish made from a natural resin with one made from a synthetic resin. Came's[4] results show that little correlation exists between the durability of spar varnishes when exposed outdoors and their durability in the accelerated weathering cycle which has been used almost exclusively at this laboratory for paints. This cycle consists in a continuous exposure to a carbon arc light and subjection to a water spray every 20 minutes. How-

[1] See Bibliography in the paper Durability Tests of Spar Varnishes, by C. L. Came, B. S. Jour. Research 4, p. 247; 1930.

[2] The kauri reduction test consists in determining the maximum amount of kauri solution which can be added to the varnish, so that after baking a film of this mixture on metal and cooling it will show no cracks on bending over a 3 mm (one-eighth inch) rod. For a full description of this test, see A. S. T. M. Standards, Pt. II, p. 358; 1930.

[3] The accelerated weathering cycle consists in exposing the varnishes to conditions simulating actual outdoor weathering, but much more severe; as intense light, water, cold, etc., so that failure can be made to occur quickly. A typical cycle is described by Came. (See paper referred to in footnote 1.)

[4] See footnote 1.

ever, it is probable that by changing the cycle as has been done by W. R. Fuller [5] results more in accord with outdoor weathering could be obtained.

The opinions of a number of manufacturers and consumers of paint and varnish in regard to the kauri reduction test and the accelerated weathering test are expressed in the replies to a questionnaire [6] sent out by a committee of the Cincinnati-Dayton-Indianapolis Paint and Varnish Production Club. All of these replies agree that neither of these tests gives completely satisfactory results, although some indicate that under certain conditions the results are satisfactory in comparing materials of the same type.

It is the purpose of this paper to describe a new method, which may be termed the photochemical embrittling test, for evaluating the durability of varnishes and to give some results which show the correlation between this test and actual weathering.

II. METHOD

The new method takes one feature from each of the two tests already described. First, the varnish films are exposed to an intense source of light, as is done in the accelerated weathering cycle, causing the photochemical embrittling, and second, the films are tested for the degree of brittleness as is done in the kauri reduction test, by bending the varnish-coated panel over a mandrel.

In detail, the test is carried out in the following steps:

1. The varnish sample is flowed on a terneplate strip. (A size of 35 by 2.5 by 0.03 cm or 14 by 1 by 0.012 inch has been found to be satisfactory.)
2. The varnish is allowed to dry in an inclined position so that the excess will flow off.
3. The 14-inch strips are cut into short chips of about 1¼ to 1½-inch length, which are appropriately marked on the back.
4. The cut strips are placed in a suitable holder, which may be made from a strip of metal about 2 inches wide and long enough to extend around the tank surrounding the carbon arc light. About one-quarter inch of one side is bent through 180° thereby forming a pocket for the chips. This holder is situated directly opposite the center of the carbon arc light and about 15 inches from it. The apparatus is the same as that used in the accelerated weathering cycle described by Walker and Hickson.[7]
5. Every hour a chip of each varnish is removed from the light, cooled to a standard temperature, and bent double over a 3 mm. (one-eighth inch) rod.
6. The chips are examined closely for signs of failure.

Two distinct types of failure have been found to occur on bending the specimens in this test. Some varnishes failed by showing long easily visible cracks of the kind obtained in the kauri reduction test. Other varnishes failed by a change which has been called whitening in

[5] H. A. Gardner, Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors (5th ed.), p. 408; 1930; Institute of Paint and Varnish Research, Washington, D. C.

[6] The Evaluation and Compilation of the Methods Used in Accelerated Testing of Protective Coatings. Cincinnati-Dayton-Indianapolis Production Men's Club. Am. Paint & Varnish Mfrs. Assoc. Circ. No. 370, pp. 548–564; Am. Paint J., 14, No. 52C, p. 25; Paint, Oil & Chem. Rev., 90, No. 18, pp. 14–17; Oil, Paint & Drug Reporter, 118, No. 19, pp. 63–4; 1930.

[7] P. H. Walker and E. F. Hickson, Accelerated Tests of Organic Protective Coatings, B. S. Jour. Research, **1**, p. 2; 1928.

this paper. This whitening is probably caused by the formation of a great many cracks, so fine that they can not be resolved by a microscope magnifying about 75 diameters. An apt comparison might be made to the bending of glass. At ordinary temperatures the glass will crack and shatter; at temperatures near the melting point it can be bent and still will remain clear and transparent; however, at an intermediate temperature the glass can be bent, but in so doing, it ceases to be transparent and reflects the light from countless newly formed surfaces, thus giving the whitened appearance.

In general, the poorest varnishes show no whitening but only the long visible cracks which on longer exposure shatter on bending. The better varnishes first become whitened and after some hours begin to crack. The condition grows steadily worse until they finally shatter. After a number of hours of light exposure the best varnishes begin to whiten. This effect gradually becomes worse and some cracking may occur after a very long exposure.

It is always desirable to run a standard varnish whose durability outdoors and elasticity after exposure to light are known along with the samples being tested, as a precaution against unknown variations, such as solarization of the glass chimney, slight changes in the radiation of the arc, possible changes in conditions at the time of bending, etc.

The only costly piece of apparatus required in this method is the carbon arc weatherometer light. It has been found possible to substitute an ordinary incandescent mazda light for the carbon arc, although a much longer exposure is required to give the same results. This comparison will be shown later in this paper.

A very useful accessory apparatus is a cabinet for obtaining any desired temperature for bending the strips. The cabinet in use in this laboratory is constructed of double windows on all sides with about three-eighths inch dead air space between the outer and inner windows. In the front of the cabinet is a board having two 6-inch holes to accommodate the operator's arms when working in the cabinet. Each hole is provided with a collapsible sleeve of insulating material so that when the arms are withdrawn, the openings can be closed. The desired temperature is obtained by running cold or hot water through a copper radiator inside the cabinet and by circulating the air with an electric fan. No difficulty is experienced in getting a temperature 10° C. below that of the room. The humidity may also be fixed, if desired, by introducing an open vessel containing a saturated salt solution of definite vapor pressure.

III. RESULTS

The type of results obtained is illustrated by tests of a set of seven varnishes submitted through the courtesy of W. R. Fuller, of the Pratt & Lambert Co., who also furnished us with their composition, kauri reduction values, and approximate outdoor durabilities. These data are given in Table 1. In order to insure an unbiased judgment, this latter information was withheld until after the completion of the tests. From the results shown in run 1 of Table 1 the varnishes were arranged in the following order: 1, 2, 3, 6, 4, 5, 7, while the order obtained from Mr. Fuller was 1, 2, 3, 4, 5, 6, 7 or, in other words, the photochemical embrittling test gave the correct order with the exception of No. 6, which was placed too low in the scale.

As stated previously the temperature at which the bending is done greatly affects the degree of cracking. This fact can be utilized to advantage by lowering the temperature of bending when it is desired to speed up a determination, as in the case of very good varnishes which do not fail in a working day, or to get an approximate idea of the number of hours that will be required before cracks will start to occur on bending at the specified temperature. This eliminates considerable useless work required in bending and examining very good varnishes in the early stages. Testing at approximately 0° C. can be done conveniently by placing the varnish specimen on a lump of ice in a closed container with the varnish side up, and after 15 or 20 minutes removing the chip and bending immediately. The results of the test made on the seven varnishes are given in run 2, Table 1 for comparison with run 1, Table 1. It will be noticed that in this determination varnish No. 6 falls in its correct position between No. 5 and No. 7.

Although the carbon arc light has been found to be satisfactory, it is quite expensive, and is now used by only a comparatively few laboratories. To make the test more available the substitution of mazda lamps for the carbon arc was tried out on the same seven varnishes. The results are shown in runs 3 and 4 of Table 1.

TABLE 1.—*Typical photochemical embrittling tests showing the effect of varying the temperature of bending and the type of lights*

Varnish No.	Run 1. A typical photochemical embrittling test									Run 2. Showing the effect of lowering the temperature of bending			Run 3. Showing the effect of substituting a 1,000-watt mazda light for the carbon arc				
	Hours in carbon arc light before bending at 22° C.									Hours in carbon arc light before bending at approximately 0° C.			Hours in mazda light before bending at 22° C.				
	0	1	2	3	4	5	6	7	8	0	2	4	3	20	26	44	68
1	O. K.	C_6	C_6	C_8	---	---	---	---	---	C_6	C_8	---	C_6	C_8	---	---	---
2	O. K.	C_2	W_6C_3	C_7	C_8	---	---	---	---	C_6	C_8	---	O. K.	C_6	C_8	---	---
3	O. K.	O. K.	W_3	W_4	W_7	W_7C_3	W_8C_6	---	---	C_3	W_7C_4	W_8C_5	O. K.	O. K.	C_1	C_5	C_5
4	O. K.	O. K.	W_1	W_3	W_3	W_6	W_7	W_8	---	O. K.	C_4	W_8C_5	O. K.	O. K.	O. K.	C_2	C_2
5	O. K.	O. K.	O. K.	O. K.	W_2	W_6	W_6	W_5	W_6C_5	O. K.	W_4	W_7	O. K.	O. K.	O. K.	O. K.	O. K.
6	O. K.	O. K.	W_2C_2	W_5C_2	W_6	W_6	W_6	W_8	---	O. K.	W_4	W_6	O. K.	O. K.	O. K.	O. K.	O. K.
7	O. K.	O. K.	W_2	W_2	W_4	W_5	W_5	W_5	W_6	O. K.	W_4	W_5	O. K.	O. K.	O. K.	O. K.	O. K.
	Strips were placed 15 inches from the light. The temperature registered by a thermometer next to the strips was 56° C.												Strips were placed 8 inches from the light. The temperature registered by a thermometer next to the strips was 60° C.				

TABLE 1.—*Typical photochemical embrittling tests showing the effect of varying the temperature of bending and the type of lights*—Continued

Varnish No.	Run 4. Showing the effect of substituting a 150-watt mazda light for the carbon arc: Hours in mazda light before bending					Compositions, kauri reductions and durabilities of the varnishes				
	Bent at 22° C.			Bent at −5° C.	Bent at 17° C.	Oil per 100 pounds of resin	Kind of oil	Kind of resin	Kauri reduction	Durability
	41 hours	65 hours	89 hours	113 hours	137 hours	*Gallons*			*Per cent*	*Months*
1	C_4	C_4	C_4	C_8	C_8	46.3	Tung	Rosin	40	3
2	C_2	C_2	C_2	C_8	C_8	45.8	do	Rosin and a small proportion of ester gum	50	3½
3	O. K.	O. K.	O. K.	C_8	C_5	45.5	do	{60 per cent rosin 40 per cent ester gum}	70	4
4	O. K.	O. K.	O. K.	C_8	C_2	49.25	Linseed and tung	Ester gum and a smaller amount of rosin	90	6½
5	O. K.	O. K.	O. K.	C_8	O. K.	63.3	Similar to No. 4, but containing additional linseed oil		120	8
6	O. K.	O. K.	O. K.	C_3	O. K.	50	Tung	Phenolformaldehyde resin	100	11
7	O. K.	O. K.	O. K.	O. K.	O. K.	50	do	Slightly more durable phenolformaldehyde resin than No. 6.	165	18+
	Strips were placed 7 inches from the light. The temperature registered by a thermometer next to the strips was 34° C.					The outdoor durability data refer to roof exposures at Buffalo, N. Y., at an angle of 45° facing south and are average figures for exposures at different periods of the year				

NOTE.—The letters C and W refer to cracking and whitening, respectively. The subscripts 1 to 8 refer to the degree of failure as follows: 1, Trace; 2, slight; 3, some; 4, definite; 5, considerable; 6, bad; 7, very bad; 8, shattered.

Here again it will be seen that the test has placed the varnishes in their correct order, although bending at a low temperature had to be resorted to in order to cause the best varnishes to fail. The time required for failure to occur is many times that required with the carbon arc. Since the 1,000-watt mazda produced a temperature near the samples which was slightly higher (4° C.) than that produced by the arc, the embrittlement of the film is not caused merely by heat. It is probably the effect of a photochemical reaction caused by a certain range of wave lengths in which the arc used had a much greater intensity than the 1,000-watt mazda lamp. The difference between the effects of the two mazda lamps is undoubtedly caused mainly by the difference in intensity of the light from the two sources, rather than a difference in spectral distribution.

The following suggested procedure might well be used in arranging a given set of varnishes in the order of their durabilities. The chips are placed in the carbon arc light and at the end of the first hour two chips of each varnish are removed. One of these chips is bent at a low temperature, say, 0° C.; the other is bent at a temperature near that of the room but preferably below 25° C. Those varnishes that crack at 0° C. are classed as poorer than those that only whiten or show no sign of failure. Thereafter the poorer varnishes by this separation are bent only at the higher temperature and are rated according to the number of hours of light exposure required before they crack. The better varnishes are bent at 0° C. until they crack and are rated by the same method. To get a finer distinction it may be necessary to select some other temperature for bending.

To illustrate the reliability of this test in rating the durabilities of a large number of varnishes, some representative results will be given. In Figure 1 are shown the results obtained with a set of 42 spar varnishes by the three quick tests [8] in comparison with the durability on outdoor exposure. The arrangement of the varnishes in the order of increasing durability shows a good distribution in the range of exposure of from 28 to 141 days before the varnish became definitely checked. This end point was considered to have been reached when checks all over the panel could easily be seen with the naked eye. The number of hours of sunshine rather than the number of days was chosen as ordinate, as this tends to eliminate discontinuities due to changes in climatic conditions. Obviously, the order of failure will be the same in both cases.

It is evident that the reliability of any test for determining durabilities should be measured by the degree with which the results obtained follow the course of those obtained by outdoor exposure. When the samples are plotted in the same order, as is done in Figure 1, the curve for each test should rise gradually from left to right. With a few exceptions this general trend is apparent in the photochemical embrittling test and the kauri reduction test, but no such relation exists for the accelerated cycle used, which consisted of exposure to a continuous carbon arc light and an intermittent water spray every 20 minutes.

By an inspection of Figure 1, it will be seen that, in general, the poorest varnishes failed by cracking only, the best varnishes failed

[8] C. L. Came, formerly of this laboratory, made the observations and determinations of the roof exposure, the kauri reduction, and the accelerated weathering cycle test.

by whitening only while the intermediate ones exhibited both types of failure.

This observation is utilized in rating the 50 varnishes of the set reported by Came.[9] These varnishes were classified into five groups as shown in Figure 2 ranging from those which failed by cracking only to Nos. 32 and 39 which showed no cracking or whitening on bending after an exposure to the light for 13 hours. Each group is divided into subgroups, underscored by a solid line, which are so similar in the embrittling test that it is impractical to try to differ-

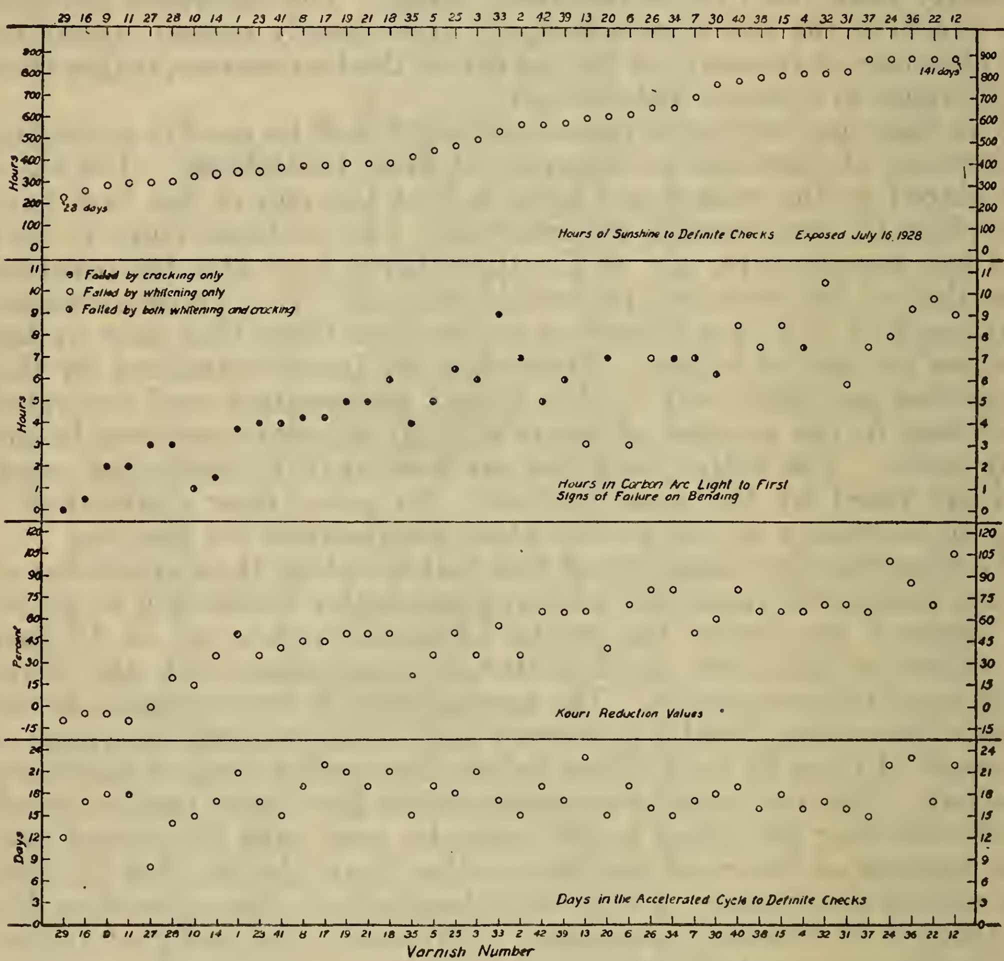

FIGURE 1.—*A comparison of the reliability of the photochemical embrittling test, kauri reduction, and the accelerated weathering cycle for the prediction of the durability of spar varnishes*

entiate between them. However the subgroups themselves can be graded in the order indicated. As may be seen from the figure, the results of the photochemical embrittling test correspond rather well with the order of outdoor durability. Unfortunately the majority of the varnishes selected for this test had approximately the same durability instead of differing in fairly even increments as is the case in Figure 1. This made a differentiation in this region difficult and likewise rather immaterial. However, these results are included since the durabilities of the varnishes have been published previously.

[9] See footnote 1, p. 73.

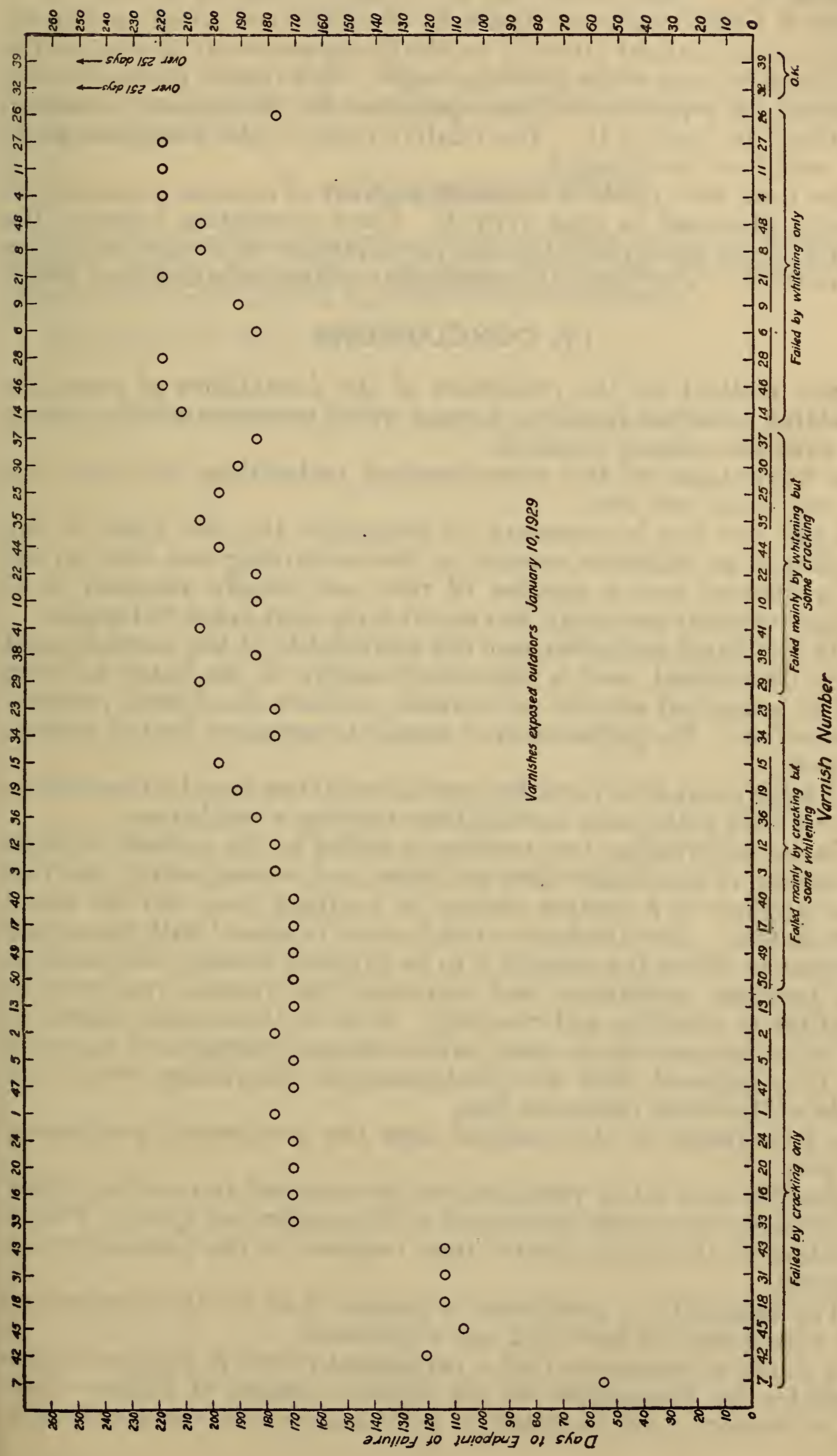

FIGURE 2.—*A set of 50 spar varnishes arranged in the order of increasing durability by the photochemical embrittling test compared with their outdoor durabilities*

The bending of the varnish strips in both of these sets was done at 24° to 25° C. When these tests were being made, the procedure was to hang a 14-inch strip vertically in the light and to cut a chip off hourly so that the light intensity on the first pieces was less than on the later pieces because of the glancing angle. Exhaustion of the samples prevented the repetition of this experiment by the present procedure as outlined in Section II. The relative order of the varnishes, however, would not be changed.

Some tests were made of a limited number of enamels consisting of pigments dispersed in spar varnish. Good correlation between the cracking in the embrittling test and the durability on outdoor exposure was observed. The pigment obscures any whitening which may occur.

IV. CONCLUSIONS

A new method for the prediction of the durabilities of varnishes and related materials has been devised which possesses certain advantages over the existing methods.

The advantages of the photochemical embrittling test over the kauri reduction test are:

1. Only one run is necessary to determine the end point in the durability of an unknown varnish by the embrittling test while in the kauri reduction test a number of runs are usually required until cracking occurs at one point, but not at 5 per cent lower reduction.

2. In the kauri reduction test the nonvolatile of the varnish must first be determined, and a calculated weight of the kauri solution added to a weighed amount of varnish to secure the desired percentage reduction. No preparation of sample is necessary for the embrittling test.

3. A large number of varnishes can be run at one time by the embrittling test with little more trouble than running a single one.

4. In the embrittling test nothing is added to the varnish, so that the question of miscibility does not arise, and, consequently, the test can be applied to a greater variety of coatings than can the kauri reduction test. Also the former test is more in accord with the actual conditions to which the varnish is to be exposed, namely, the sunlight which hardens, embrittles, and contracts the varnish rendering it susceptible to checking and cracking. Even in those cases where the kauri reduction test can be used, as oleoresinous varnishes of the same type, it is believed that the photochemical embrittling test is as reliable as the kauri reduction test.

The advantages of this method over the accelerated weathering cycle are:

1. Results on a set of varnishes can be obtained in one day, while approximately two weeks is required in the accelerated cycle. This is in addition to the much shorter time required in the preparation of the panels.

2. The reliability of prediction is greater than for the accelerated cycles with which we have had any experience.

3. A minor advantage is that a permanent record in the bent chips is available for comparison at the different stages of failure while notes or memory must be relied on for comparison in the accelerated cycle.

The disadvantages of the photochemical embrittling test are:

1. It predicts checking only. While this is probably sufficient for varnishes, it is not sufficient for pigmented coatings which also fail by chalking, fading, loss of gloss, etc.

2. The end point is not always definite as in the kauri reduction test and considerable experience and judgment may be required for an accurate prediction.

V. ACKNOWLEDGMENT

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