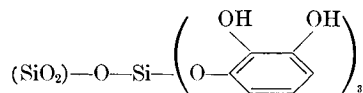


Figure 1.

persed antioxidants which may diffuse through the solid polymer show a linear relationship between $1/T$ and the induction period, but for antioxidants of large particle size, such as carbon black, this relationship diverges from linearity approximately at the polymer melting range.

Nonblack antioxidants in the particle range of carbon black have now been prepared by chemically bonding antioxidant groups to an inert particle surface. Silicon dioxide particles (10 g.) having an average mean diameter of 200 Å, approximately that of carbon black used to inhibit photo-oxidation, is reacted in carbon tetrachloride solution (210 cc.) with silicon tetrachloride (10 cc.). After refluxing for 2 hr., the unreacted halide is distilled off with about 10 cc. of the solvent. Pyrogallol (10 g.) is added and the reaction mixture refluxed for an additional 2 hr. The pale lavender complex which forms and may be represented schematically



is separated by filtration, washed twice with benzene, and dried in a vacuum desiccator. A similar complex has been prepared in which catechol was the phenolic component of the reaction. The organic surface coatings could not be extracted from the silica particles with organic solvents, and, on pyrolysis, the treated silica had a volatile loss several per cent higher than that of silicon dioxide comparably conditioned.

Approximately 3 g. of the complex was added to 100 g. of branched polyethylene by mill massing of the molten polymer. In contrast to silicon dioxide, which showed no antioxidant effectiveness at 140°C., the pyrogallol complex gave an induction period of 50 hr. and the catechol complex, 105 hr. As shown in Figure 1, the temperature effect with these complexes is similar to that of carbon black. In each instance the relationship between log of the induction period and $1/T$ diverges from linearity near the polymer melting range.

These data support the conclusion that functional groups on the carbon surface are responsible for antioxidant effectiveness. Attaching similar reactive groups to the surface of silicon dioxide produces an effective antioxidant. Furthermore, the effect of temperature on the oxidative stability of polyethylene inhibited with these complexes is similar to that observed when carbon black is the anti-

oxidant. The nonlinear temperature dependence is consistent with the proposal that the average distance which a propagating radical must travel to be terminated on the carbon surface is much greater in the melt than in a solid, semicrystalline polymer.

References

1. Biggs, B. S., and W. L. Hawkins, *Modern Plastics*, **31**, 121 (1953).
2. Hawkins, W. L., M. A. Worthington, and F. H. Winslow, *Proceedings of the Fourth Conference on Carbon*, 1960, p. 63.
3. Studebaker, M. L., *Rubber Chemical Technol.*, **30**, 1438 (1957).
4. Hallum, J. V., and H. V. Drushel, *J. Phys. Chem.*, **62**, 110 (1958).
5. Garten, V. A., and D. E. Weiss, *Revs. Pure and Appl. Chem. (Australia)*, **7**, 67 (1957).
6. Hawkins, W. L., W. Matreyek, and F. H. Winslow, *J. Polymer Sci.*, **41**, 1 (1959).

W. L. HAWKINS
W. MATREYEK
F. H. WINSLOW

Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey

Received January 4, 1961

The Gelation Point of Alkyd Resins

The paper by M. Jonason on this subject¹ deals with a special case of the calculation of gelation points in condensation polymerizations, where reacting groups of a given species (as, e.g., hydroxyl, carboxyl, amino) do not all react at the same rate.

This general problem was solved in 1957 by Case.² The results of Jonason do not seem to agree with those of Case. The analysis can also be carried further than has been done by either of these workers.

If an anhydride A-B reacts with a triol C, the condition of gelation, in Case's notation is

$$2\beta 2\gamma / (\alpha + \beta) = 1$$

where α , β , γ are the fractions of A, B, and C groups reacted, the A group reacting first.

The result given by Jonason, by simplification of his eq. (12) is

$$2\alpha\beta 2\gamma / (\alpha + \beta) = 1$$

which is the result obtained by Case for the reaction of an unsymmetrical acid A-B with a triol C.

The discrepancy arises because Jonason has not distinguished between the anhydride and acid cases. In the former the anhydride group (A) must react first, before a B group can react, and this alters the statistical considerations.

For alkyd resins based on phthalic anhydride, reaction to the half-ester is in fact so rapid that α can be taken as unity. The two formulas will hence give the same numerical result for such polymers; but this is not general.

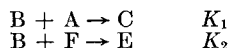
The discussion by Jonason of the reactivity of carboxyl groups calls for comment. An extreme reluctance of aromatic carboxyls to react is inferred from some results on

acid-catalyzed esterifications at moderate temperatures. These are hardly relevant. There is indeed a shortage of reliable rate data for the alkyd reaction for oil-modified systems, esterified at, say, 180–230°C. The work of Wekua and Reiser² and Wekua and Klausch⁴ does, however, show that, although a phthalic carboxyl does esterify more slowly than a fatty acid carboxyl, there is no over-large ratio of rate constants. At the temperatures usually employed we can adopt 10^{-2} and $10^{-2.5}$ (mole l.⁻¹ sec.⁻¹) as rate constants for fatty and phthalic acids in esterification with glycerol.

Jonason gives no indication as to how the values of α , β etc. (his P_A , P_B , etc.) may be obtained from kinetic data, and is content with various assumptions. Solutions of this problem have been given by Case. For parallel reactions Case uses an approach basically due to Geitel⁵ and for consecutive reactions a method due to Frost and Schwemer.⁶ This latter applies only to balanced reactions.

Both cases can be covered by a device due to McMillan,⁷ which can be extended to cover reversible polyesterifications.

Consider the reaction of a symmetrical dibasic acid A and a fatty acid F with a symmetrical triol B:



Then

$$\begin{aligned} dB/dt &= -K_1ab - K_2bf \\ dA/dt &= -K_1ab \\ dF/dt &= -K_2bf \end{aligned}$$

where a , b , f are the fractions of A, B, F unreacted (i.e., $a = (1 - \alpha)$ etc.)

Putting

$$\theta = \int_0^t bdt$$

we obtain

$$da/d\theta = -K_1a \quad \text{and} \quad df/d\theta = -K_2f$$

so that

$$a = a_0 \exp \{-K_1\theta\} \quad (1)$$

and

$$f = f_0 \exp \{-K_2\theta\} \quad (2)$$

where a_0 and f_0 are initial values.

There will be a complicated expression for b , but the method leads readily to the degree of acid reaction at gelation.

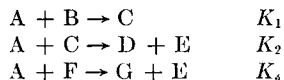
If the system is balanced, then at gelation, following Case:

$$2(2\alpha + \zeta)\alpha^2/3(\alpha + 1/2\zeta) = 4\alpha^2/3 = 1$$

and hence $\alpha = 0.86$. Taking K_1 as $10^{-2.5}$, eq. (1) may be solved for θ . Then taking K_2 as 10^{-2} , eq. (2) may be solved to give $f = 0$, $\zeta = 1$.

The degree of acid reaction at gelation is, hence: $(1.72 + 1)/3 = 0.91$. For equal rates p (gel) acid will be 0.85.

The same approach may be applied to an anhydride reaction, where B-C is an anhydride reacting with a triol A, B reacting first, and a fatty acid F being present:



If we put $\theta = \int_0^t adt$, we can derive:

$$\begin{aligned} da/d\theta &= -K_1b - K_2c - K_3f \\ db/d\theta &= -K_1b \\ dc/d\theta &= -K_1b - K_2c \\ df/d\theta &= -K_3f \end{aligned}$$

Taking the first step of half-ester formation as very fast, with $b = 0$, we obtain

$$f = f_0 \exp \{-K_3\theta\} \quad (3)$$

$$c = b_0 \exp \{-K_2\theta\} \quad (4)$$

so that the acid value at gelation can again be derived.

For a balanced oil-modified alkyd at gelation,

$$2\alpha 2\gamma/(1 + \lambda + r\zeta) = 1$$

where r is the ratio of F to B groups ($= 1$) and ζ is the fraction of F groups reacted.

Since $3\alpha = 1 + \gamma + \zeta$, $4\gamma/3 = 1$, and $\gamma = 3/4$. Hence $C = 1/4$, and eq. (4) can again be solved for θ , and eq. (3) can be solved for f , and thence ζ . Using the rate constants adopted earlier, we get $\zeta = 1$, and the degree of acid reaction at gelation is $(1 + 0.75 + 1)/3 = 0.92$.

Other factors affecting the gel point are cyclization and polymerization of drying oil. These are believed to be small, but they cannot be treated quantitatively at this time.

An effect that is not small is that due to reversibility, which had not hitherto been discussed.

Both stages of the alkyd reaction with phthalic anhydride are reversible.

The reversibility of the second polycondensation stage was recognized by Schulz.⁸ It has been found by Wiltshire⁹ that the equilibrium constant for this stage is about $1/3$, so that, unless substantially all water of reaction is removed, gelation cannot occur. Unless the amount of water is known, and an equilibrium is assumed, however, no calculations relating to gel point can be made. The equilibrium constant in the first stage is about unity⁹ and the equilibrium is very rapidly attained. From the data of Shkolman and Zeidler¹⁰ it appears that K_1 (at the likely temperature of alkyd resin production, about 220°C.) is also unity.

The kinetic equations describing the system (if all water is removed),



can be solved by the McMillan method noted earlier, but complicated expressions result. It is also necessary in this case to find the parameter θ experimentally, and it is of course easier to determine a gel point.

However, the data given here indicate that reversibility in both stages of the alkyd reaction will be a considerable factor in retarding gelation, and this factor does not seem to have been recognized. It will of course be allowed for in empirical factors which have been obtained, in order to account for the behavior of phthalic anhydride.

By knowing that the first stage equilibrium is rapidly established, and making the reasonable assumption that all the (equilibrium) anhydride and fatty acid are consumed, the effect of reversibility in gel point can, however, be estimated. We will consider two cases:

(a) A triol A reacting in balanced proportions with an anhydride B-C, B reacting first. For gelation, $2\alpha 2\gamma/\beta + \gamma = 1$ and since $\beta + \gamma = 2\alpha$, $\gamma = 1/2$ at gelation. With an equi-

librium constant of unity, the equilibrium concentrations of B and C are 0.7 and 0.6. By taking therefore β gel as 0.7, the degree of acid reaction at gelation is $0.7 + 0.5/0.7 + 0.6 = 0.92$, as compared with 0.75 for the irreversible case.

(b) A triol A reacts with an anhydride B-C and a fatty acid F in balanced proportions. For gelation $2\alpha + 2\gamma/\beta + \lambda + \zeta = 1$ so that $\gamma = 3/4$ at gelation. In the first stage $3\alpha = \beta + \gamma$, so that the equilibrium concentration of C is $3/4$, giving an equilibrium concentration of B of $(1 - 0.75/2)$ or 0.625. If all B and F are consumed, β and ζ are 0.625 and 1 at gelation. The degree of acid reaction at gelation is, therefore, $0.75 + 0.625 + 1/0.75 + 1 = 1$, compared with 0.92 for the irreversible case.

If the anhydride is taken as a dibasic acid, then gelation will be calculated to occur at 0.85.

These calculations illustrate the considerable error likely to be introduced by neglect of reversibility and by treating phthalic anhydride as a dibasic acid.

References

1. Jonason, M., *J. Polymer Sci.*, **4**, 129 (1960).
2. Case, L. C., *J. Polymer Sci.*, **26**, 333 (1957).
3. Wekua, K., and W. Reiser, *Farbe u. Lack*, **58**, 297, 345 (1952).
4. Wekua, K., and W. Klausch, *ibid.*, **59**, 85 (1953).
5. Geitel, A. C., *J. prakt. Chem.*, **55**, 429 (1897).
6. Frost, A. A., and W. D. Schwemer, *J. Am. Chem. Soc.*, **74**, 1268 (1952).
7. McMillan, W. G., *ibid.*, **79**, 4838 (1957).
8. Schulz, G. V., *Z. physik. Chem.*, **A182**, 127 (1938).
9. Wiltshire, J. P. (unpublished work).
10. Shkolman, E. E., and I. I. Zeidler, *J. Appl. Chem. U.S.S.R.*, **23**, 79 (1950).

H. S. LILLEY

Research Department, Paints Division
Imperial Chemical Industries Ltd.
Wexham Road, Slough, Bucks, England

Received April 17, 1961

Rate of Oxidative Stress Relaxation and the Extension

A number of experimenters¹⁻³ have reported the rate of thermal oxidative stress relaxation of sulfur vulcanizates of natural rubber as independent of the extension given to the strip, up to moderately high values. Similar independence has also been reported⁴ for a sulfurless peroxide vulcanizate in photochemical aging. Some recent work of Mullins and Watson⁵ on hot mastication of unvulcanized natural rubber indicated, however, that stress markedly accelerates the oxidative scission of the rubber molecules even when inadequate to rupture the chains mechanically as during cold mastication. The lack of dependence of rate of relaxation on extension up to about 300% is important practically if stress relaxation is used to follow oxidative degradation and, since it is believed⁶ that sulfurless vulcanizates, at least, degrade by the same mechanism as the unvulcanized rubber, it appeared that a further check would be worthwhile for the case of thermal degradation of a peroxide vulcanizate.

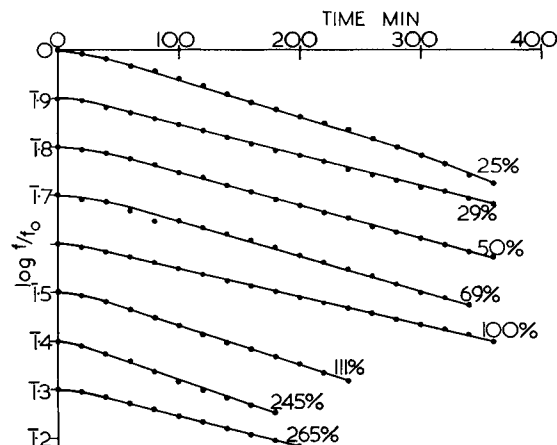


Fig. 1. Stress relaxation in air at 100°C. of a natural rubber peroxide vulcanizate at varying elongations. The figures against the curves give the corresponding extensions.

A natural rubber vulcanizate was prepared from the following recipe: highly purified rubber (U. S. Rubber Co.) 100, dicumyl peroxide 0.75, and HAF Black 5, cured 60 min. at 153°C. The cure time was extended to reduce residual peroxide and, in fact, corresponds to about 8 half-lives. Stress relaxation was carried out without extraction which, it was considered, might introduce inhomogeneity. Without the small loading of black the more highly extended strips tended to break after very brief heating.

The results of the continuous stress-relaxation measurements at 100°C. in air are given in Figure 1. There is some scatter in the observed rates but there is no indication of a trend of rate with extension over a range from 25% to 265%.

The lack of any apparent effect of stress on rate in these experiments is not necessarily in conflict with the results in hot mastication, as the elastic strains exerted during mastication, although unknown, are probably considerably higher. The strain energy for moderate to high extensions will rise at least as rapidly as the square of the extension ratio, and any contribution made by this energy to the activation energy for oxidation will rise similarly.

References

1. Tobolsky, A. V., I. B. Prettyman, and J. H. Dillon, *J. Appl. Phys.*, **15**, 380 (1944).
2. Berry, J. P., *J. Polymer Sci.*, **21**, 505 (1956).
3. Scanlan, J., and W. F. Watson, *Trans. Faraday Soc.*, **54**, 740 (1958).
4. Dunn, J. R., J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, **54**, 730 (1958).
5. Mullins, L., and W. F. Watson, *J. Appl. Polymer Sci.*, **1**, 245 (1959).
6. Dunn, J. R., J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, **55**, 667 (1959).

L. J. MAISEY
J. SCANLAN

Rubber and Plastics Research Association of Great Britain,
Shawbury, Shrewsbury, Shropshire, England

Received January 13, 1961