Silicone-Alkyd Copolymers and Their Application to High-Temperature Surface Coatings

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ALTHOUGH THE NUMBER of theoretically possible organo-silicon copolymers is large, only silicone-alkyd copolymers have received much study and investigation. Probably this is due to the complementary properties which the two classes of resins possess, making their copolymers more useful in high-temperature surface finishes.

Silicone-alkyds made their first appearance in the patent literature at the end of 1946 and in the journal literature in 1947. Ever since they have been increasingly discussed in many publications. Among the articles are those of Emblem (*5*), Glaser (*6*), Stebleton and Hedlund (*18*), Rose (*14*), Brady (*1, 2*), and Hiles, Golding, and Shreve (*8*). Among the patents are those of Bunnell (*3*), Hatcher and Bunnell (*7*), Libbey-Owens-Ford Glass Co. (*10*), McLean (*11*), Smith and others (*15*), Sowa (*16*), and Speier (*17*).

This investigation was primarily concerned with a basic study of the effects of the alkyd and silicone components on the properties of the copolymers, particularly as they bear on their use in high-temperature surface coatings.

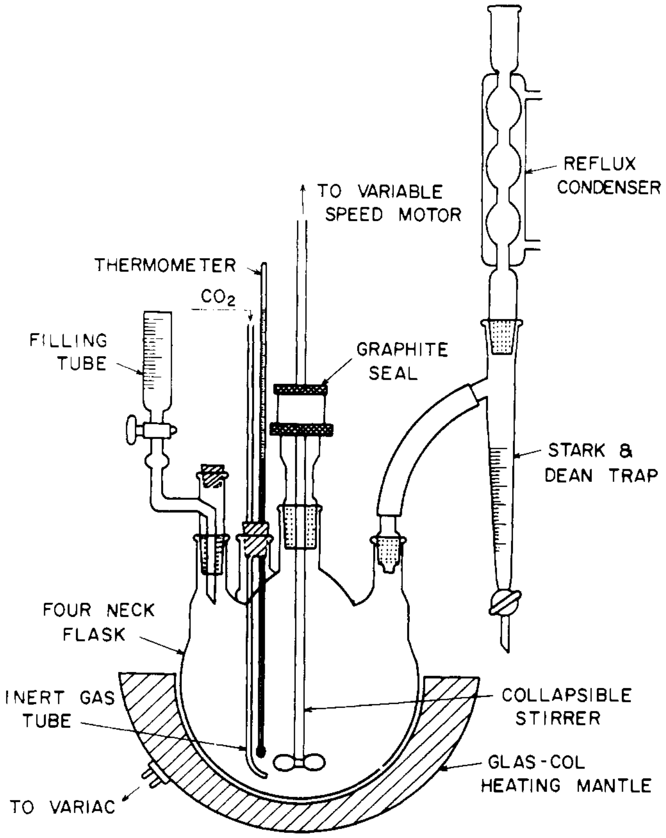

Figure 1. Apparatus for preparation of resins

EXPERIMENTAL

Apparatus. The alkyd resin intermediates were prepared by conventional methods, using the fatty acid–solvent reflux technique. The setup is shown in Figure 1.

For copolymerization with the silicone a fractionating column fitted with a Kornblum condenser replaced the reflux condenser (Figure 2). The column was provided with a thermometer and auxiliary connections for varying the reflux ratio. The alcohol liberated from the copolymerization reaction was collected in a graduated funnel.

Procedure. Silicone-alkyd copolymers were prepared by weighing the desired quantities of the polyol and dibasic and monobasic acids into the reaction flask. A selected solvent was added (5 to 10% of the weight of reactants) and the mixture heated rapidly to obtain a steady reflux between 180° and 232° C. under an inert atmosphere and continuous agitation until the acid number was reduced to 10 or lower. The heating was then discontinued, and the resin was allowed to cool to about 160° C. Meanwhile, the reflux condenser was disconnected and replaced by the fractionating column.

The desired amount of silicone intermediate was added, stirring was resumed, and heating was adjusted to permit a gentle reflux in the fractionating column. When the head thermometer showed a temperature within 1° to 2° of the boiling point of the alcohol, the latter was allowed to flow to the graduated funnel. As the reaction proceeded, the initially incompatible mass cleared and within 30 to 40 minutes became homogeneous. The reaction was continued until near gelation. At this point, the heat source was removed, and enough solvent was added to form a varnish of 60 to 70% total solids. The rate and extent of copolymerization were measured by the amount of alcohol collected in the funnel.

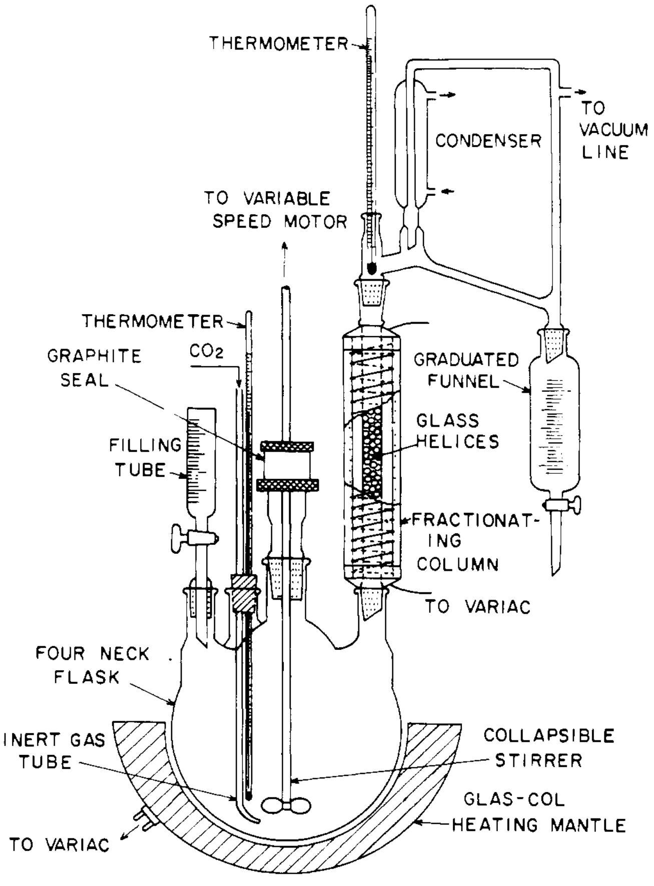

Figure 2. Apparatus for copolymerization

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Formulations. All formulations were based on chemical equivalencies. This was a deviation from the standard methods used in the coatings industry, where formulations are primarily based on percentage oil length. Earhart (*4*) has claimed that practical alkyds cannot be formulated based on concepts fashioned around theoretical proportions. Such formulations are of academic interest, and considerable difference exists between theory and practice. However, in this study the attempt was made to reconcile theory and practice. The discussion of results is based on correlations obtained by the treatment of variables on a chemical equivalency basis as well as percentage weight basis.

Evaluation and Testing Methods. The silicone-alkyd resins were evaluated as varnishes and in enamels by a series of tests selected to give satisfactory indication of the physical characteristics and fundamental and service properties of the copolymers.

Enamels were made with rutile titanium dioxide, using a pigment to resin ratio of 1 to 1 and 2 to 3. The pastes were passed twice through a laboratory three-roll mill. The ground pastes were thinned with a 1 to 1 xylene-butyl acetate mixture to a viscosity of 20 to 25 seconds (No. 4 Ford cup). After centrifuging to remove oversize, the enamels were sprayed on cold-rolled steel, black iron, and plate glass panels.

For improved adhesion of enamel films, the substrate surface preparation was very important. The best results were obtained when the substrate surface was degreased, slightly roughened with steel wool, moistened with an organic solvent, rinsed throughly, and heated for about 5 minutes in an oven at 200° C. before the enamel was sprayed. Various phosphate treatments and preparations recommended by other investigators or the trade were less satisfactory.

Parameter Limits of Alkyd and Silicone Ratios. The limiting ratios of the silicone and alkyd components were determined in a system using phthalic anhydride, 2-ethyl hexanoic acid, trimethylolethane, and phenyl ethoxy polysiloxane. Table I summarizes the resin compositions and their properties as evaluated by a series of tests on the varnishes and enamels made therefrom.

Processing time varied mainly in the alkyd esterification. Formulations with a high dibasic to monobasic acid equivalents ratio (D/M) reacted more rapidly, and the polyesters were of higher viscosity when ready for copolymerization.

Viscosity increased with increase in both the D/M ratio and silicone content. Figure 3 shows that in varnishes of low silicone content the increase in viscosity was predominantly determined by the dibasic acid, while in varnishes of high silicone content, the silicone was the determining factor.

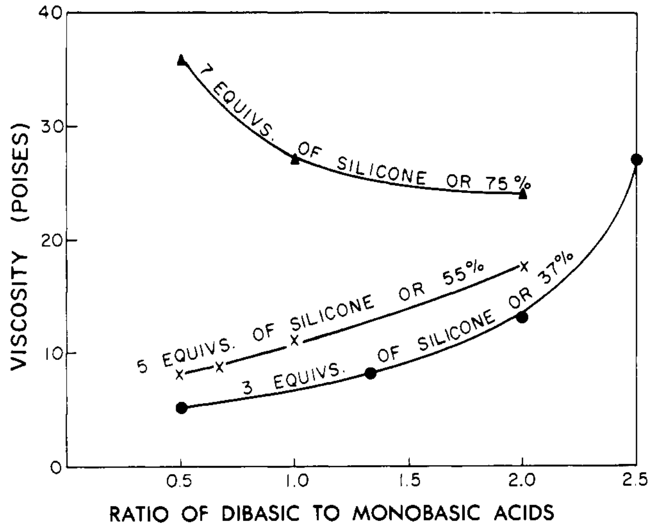


Figure 3. Change in viscosity with D/M ratio and different silicone contents

The percentage weight loss of resins at 232° C. (450° F.) was used as a comparative measure of their relative heat stabilities. As seen in Figure 4, the percentage weight loss decreased with increase in silicone content. This was expected because the silicone constituent is the more heat stable and extends a protective effect on the alkyd portion. At constant silicone content, the influence of the alkyd components is shown in Figure 5.

Gloss was a function of the D/M ratio and the silicone content. Figure 6 shows that gloss increased sharply with increase in D/M ratio, reaching a maximum at values close to two. As the percentage silicone increased, the gloss steadily increased without appreciable shift in D/M value up to about 55 to 60% silicone content. Above this value, the effect of the silicone constituent became predominant, and maximum gloss shifted to lower values of D/M ratios. Figure 7 shows the effect of percentage silicone content on gloss at constant D/M ratios. Figure 8 shows that hardness

Table I. Varnish and Enamel Propeties of Resins Prepared to

	Composition and Processing				Varnish Properties[a]						
Resin No.	% silicone[c] (25% ethoxy)	% M[d] (EHA)	D/M[d] PA/EHA equivs.	Approx. cooking time, min.	% solids	Acid no.	Color (Gardner)	Viscosity Gardner	Viscosity Poises	% wt. loss Hr. at 232° C. 24	% wt. loss Hr. at 232° C. 50
30	38	24	2.50	270	71.0	6.9	2-3	Z_1	27.0	41.0	44.9
31A	37	26	2.00	335	69.4	7.1	2-3	X	12.9	40.5	45.1
32	37	35	1.33	360	71.9	4.4	2-3	V	8.0	45.2	48.2
17	35	52	0.50	450	74.8	16.4	2-3	S	5.0	. . .	. . .
33	46	33	1.00	390	66.8	5.8	2-3	U^+	7.0	37.0	39.4
34	58	18	2.00	350	67.7	4.1	2-3	Y	17.5	22.2	25.3
35	56	27	1.00	385	66.0	4.7	2-3	W	10.8	26.8	29.3
36	55	32	0.67	420	65.5	3.8	2-3	V	8.8	27.3	29.6
6A	54	35	0.50	440	69.0	4.4	2-3	T	8.0	. . .	. . .
37	66	21	1.00	390	69.4	4.8	2-3	Z	22.8	15.2	17.5
38	76	10	2.00	315	67.8	3.9	3-4	Z^+	24.0	8.0	10.1
39	75	15	1.00	330	67.5	4.4	3-4	Z_1	27.0	10.4	12.0
40	74	20	0.50	420	66.9	3.8	3-4	Z_2	36.2	14.0	16.2

[a] 66.7% solids.
[b] Pigment to resin ration was 1.0 for all samples.
[c] Phenyl ethoxy polysiloxane.
[d] M = monobasic acid, D/M = dibasic/monobasic acid, PA = phthalic anhydride EHA = 2-ethylhexanoic acid.

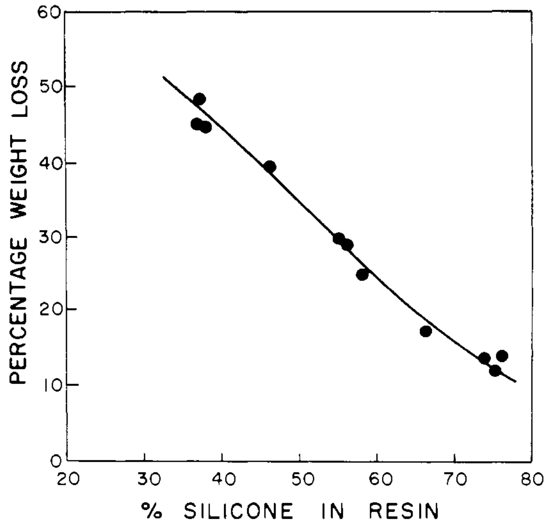


Figure 4. Percentage weight loss of resins after heat exposure of 50 hours at 232° C.

increased with increase in D/M ratio. The contribtuion of the silicone constituent toward hardness is less than that of the alkyd constituent.

These results indicate that when the silicone component is incorporated into the copolymer in less than 30 to 35% by weight of product, no significant improvement in thermal stability is noted. But, when the percentage silicone exceeds 65 to 70%, the effect of the alkyd component becomes negligible, and the copolymer begins to suffer from the properties inherent in the pure silicone. The optimum silicone-alkyd compositions ranged from 50 to 60% silicone content, using an alkyd having a D/M ratio close to two. Such compositions showed superior gloss, color and color retention, adhesion, alkali and solvent resistance, and longer heat life.

Effect of Monobasic Acids. The monobasic acid used in alkyd preparation has a pronounced effect on gloss, flexibility, adhesion, and integrity of the varnish or enamel films, so eight monobasic acids were selected to investigate their effect on the properties of the copolymers: *n*-butyric, *n*-caproic, 2-ethylhexanoic, pelargonic, lauric, stearic, benzoic, and *tert*-butylbenzoic. The experiments were formulated with a D/M ratio of 2 and a silicone content of 55%. The dibasic acid used was phthalic anhydride, the silicone was phenyl ethoxy polysiloxane of 25% ethoxy content, and the polyol was trimethylolethane. The resins prepared were tested in the usual manner and the results are tabulated in Table II.

Figure 9 shows how the percentage weight loss increased with increase in acid chain length. This is a relative measure of the decomposition extent of the resins. Such a decomposition was manifested in many enamel properties. For example, Figure 10 shows that gloss and gloss retention decreased slowly with increase in chain length up to caproic acid. At higher chain lengths, the decrease in gloss became so pronounced that it outweighed the increase in flexibility contributed by the longer chains, and as a result, the heat life of the films became increasingly shorter. The increase in yellowness of the enamel film with heat (Figure 11) is another aspect of the same phenomenon. Figure 12 shows the marked effect of the monobasic acid on the heat life of the enamel film at 232° C. 2-Ethylhexanoic, benzoic,

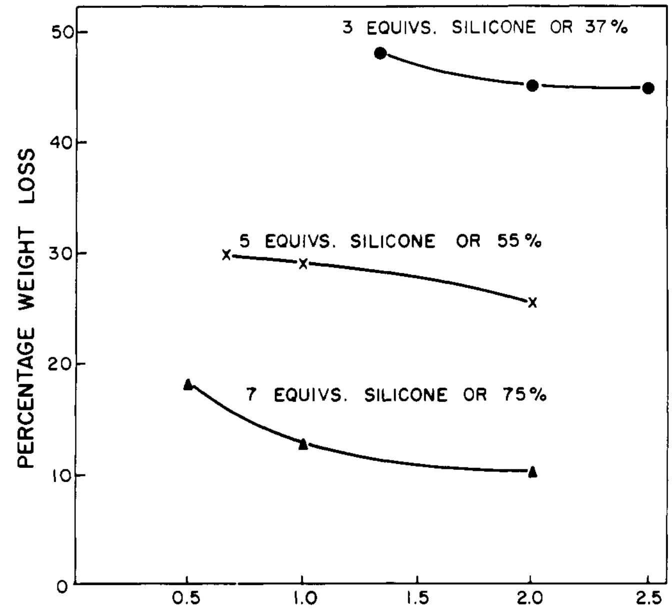


Figure 5. Percentage weight loss vs. D/M ratio

Determine Parameter Limits of Silicone and Alkyd Components

Viscosity		Enamel Properties[b]												
		Gloss					Yellowness		Hardness					
		Hr. at					Hr. at 200° C.		Hr. at				Relative heat life[e]	Alkali resistance
Ford 4 sec.	Poises	200° C. 1	200° C 40	200° C. 100	232° C. 40	232° C. 100	1	100	200° C. 1	200° C. 40	200° C. 100	232° C. 40		
30.0	0.80	87	84	82	71	. .	0.034	0.023	25	38	39	34	7	80
29.9	0.80	91	84	84	65	. .	0.044	0.023	16	26	38	34	8	96[f]
30.7	0.85	87	80	78	60	. .	0.065	0.083	6	33	36	34	12	96[f]
30.0	0.80	13	0	. .	. .	. .	0.040	. . .	. .	. .	. .	. .	13	50[g]
29.6	0.80	93	83	79	. .	. .	0.045	0.025	10	31	33	. .	11	96
31.0	0.85	104	102	95	89	88	0.034	0.034	30	35	35	32	1	96[f]
31.0	0.85	92	82	85	75	79[h]	0.044	0.034	18	28	30	. .	3	50
27.0	0.70	96	84	83	. .	. .	0.034	0.034	14	28	29	. .	9	96
32.0	0.90	70	75	65	. .	. .	0.034	0.070	7	24	28	. .	10	96
31.0	0.85	93	89	90	88	85[h]	0.045	0.045	18	30	32	28	2	50
31.0	0.85	91	86	85	84	83[h]	0.044	0.045	28	28	31	. .	5	30
31.0	0.85	96	96	93	92	87[h]	0.034	0.035	26	28	29	28	4	25
30.5	0.80	80	78	83	77	. .	0.044	0.056	14	18	28	. .	6	5

[e] 1 is best.
[f] Intact.
[g] Decrease in gloss.
[h] Measurements made on cracked film.

Table II Varnish and Enamel Testing Results Which Show Effect of Monobasic Acid

Composition and Processing				Varnish Properties						Enamel Properties[a]											
						% Weight loss, Hours at 232° C.				Gloss Heating Hours at							Yellowness Hours at		Hardness Hours at		
										200° C.	232° C.	232° C.	232° C.	232° C.	260° C.	260° C.	200° C.	232° C.	200° C.	232° C.	
Resin No.	% silicone[c]	Monobasic acid	% M[d]	Acid No.	% solids	25	50	75	100	1	20	40	70	95	25	50	1	20	1	20	Heat life, Hours
60	55	Butyric	15.4	5.1	62.6	21.0	24.3	26.7	28.4	95	92	91	89	88	83	82	0.022	0.033	30	34	264
61	55	Caproic	18.0	7.0	62.2	25.4	29.3	31.4	33.2	93	88	85.5	83	82.5	80	75	0.011	0.011	29	41	144
62	55	2-Ethyl hexoic	19.8	8.2	70.4	27.4	30.2	32.6	34.6	100	97.5	94.5	92	91.5	[b]	[b]	0.022	0.022	30	44	130
63	55	Pelargonic	20.7	5.0	68.1	28.6	31.9	34.1	35.9	90	82	78.5	75	47[b]	[b]	[b]	0.033	0.122	18	36	70
64	55	Lauric	23.1	9.4	70.2	32.3	35.7	37.7	39.5	88	77	71	[b]	[b]	[b]	[b]	0.068	0.20	34	[b]	40
65	55	Stearic	24.5	2.0	71.1	34.5	36.2	38.3	39.8	84	75.5	67.5[b]	[b]	[b]	[b]	[b]	0.092	0.25	34	[b]	20
66	55	Benzoic	18.3	5.4	71.3	17.3	20.5	22.5	24.2	102	99	98	96.5	96	90	88	0.022	0.033	46	48	280
67	55	*tert*-Butyl benzoic	22.0	7.1	68.2	16.2	20.7	21.5	22.0	98	95	86	80	80	[b]	[b]	0.022	0.022	56	58	95

[a] Pigment to resin ratio was 2/3 for all samples.
[b] Film was cracked.
[c] As charged, based on total resin.
[d] As charged, based on alkyd.

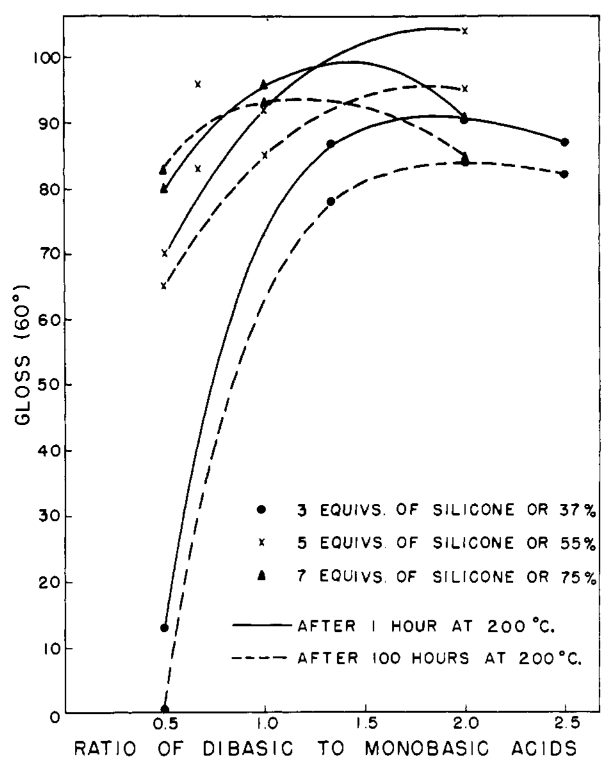


Figure 6. Effect of D/M ratio on gloss

and *tert*-butylbenzoic acids do not correlate with the regular trend exhibited by the normal-chain acids.

To determine whether the decomposition was attributable to simple pyrolysis of the polymer molecule or to oxidation of one form or another, steel panels were spraycoated with a number of enamels. The panels were cured for 1 hour at 205° C., then baked for 48 hours at 232° C.—half in a circulating air oven at atmospheric pressure and half in a tubular quartz oven under a pressure of 1×10^{-4} mm. The results (Table III) proved that the decomposition was an oxidation phenomenon regardless of the acid used. In the absence of air, copolymers of the longest acid chain length retained high gloss, color, good adhesion, and full film integrity.

Thus, flexibility and thermal stability, two essential properties in high-temperature surface coatings, were found to vary inversely with chain length of the monobasic acid. While increasing chain length tended to increase the flexibility of the resin film, the greater oxidative decomposition of the longer-chained acids at 232° C. and above resulted in inferior gloss, color, and color retention, and shorter heat life. On the other hand, the greater thermal stability attained with decrease in the monobasic acid chain length produced products of inferior flexibility and limited compatibility.

Benzoic acid appeared to combine the largest number of desirable properties. Its chief drawback was its contribution of a certain degree of brittleness to the enamel film, which limited its flexibility and impact resistance.

Effect of the Polyol. Completely eliminating the monobasic acid constituent of the alkyd and substituting difunctional glycols for trimethylolethane [2-(hydroxymethyl)-2-methyl-1,3-propanediol] decreased the rates of esterification,

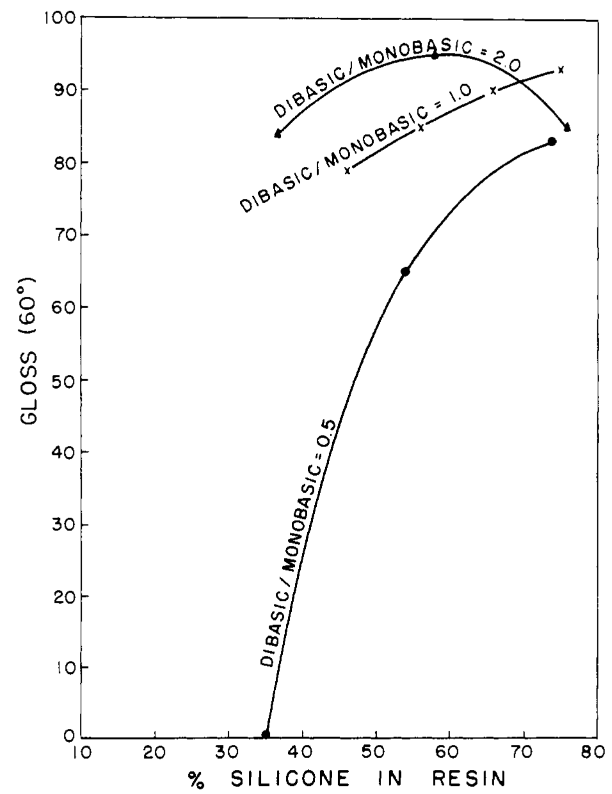


Figure 7. Effect of percentage silicone on gloss

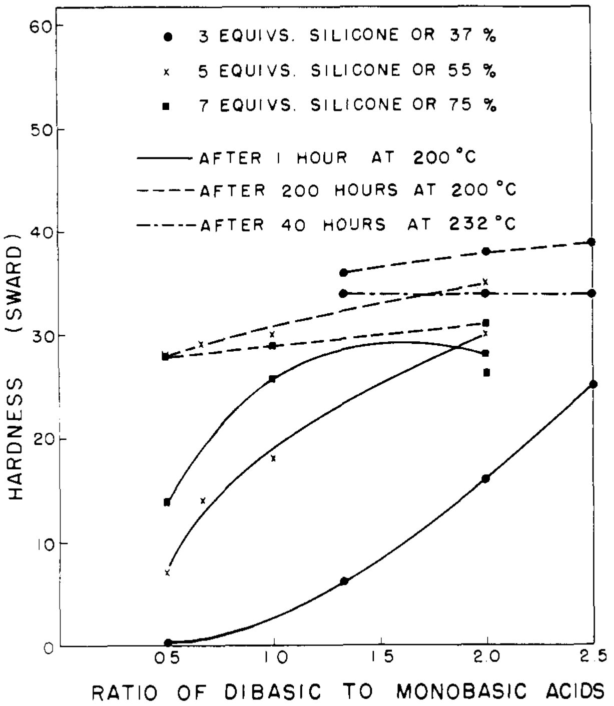


Figure 8. Effect of D/M ratio on hardness

Table III. Gloss and Color Changes in Air vs. in Vacuum

Monobasic Acid in Alkyd	Gloss after 48 Hr. at 232° C.		Yellowness after 48 Hr. at 232° C.	
	In air	In vacuum	In air	In Vacuum
2-Ethylhexanoic	89	92	0.0225	0.0227
Benzoic	88	90	0.0225	0.0140
Lauric	70[a]	90	0.1820	0.0227
Stearic	58[a]	85	0.2580	0.0227

[a] Film was cracked.

copolymerization, and curing. The flexibility of silicone-alkyd copolymers containing the difunctional glycols was greater than those of comparable copolymers containing trimethylolethane. Thermal stability decreased with increase in glycol chain length. Triethylene and diethylene glycols produced silicone-alkyd enamels which suffered from inferior thermal stability and other undesirable properties. Figure 13 shows the gloss and gloss retention at 232° C. of products made from different glycols. Ethylene, propylene (1,2-propanediol), and trimethylene (1,3-propanediol) glycols produced resins having fair enamel properties. Of the six glycols investigated, neopentyl glycol (2,2-dimethylpropanediol) exhibited the best properties in the enamels. Its incorporation with trimethylolethane may have desirable effects on the flexibility of the copolymers if the desired service temperature is 232° C. or below. The limited thermal stability of the glycols precludes their use at higher service temperatures.

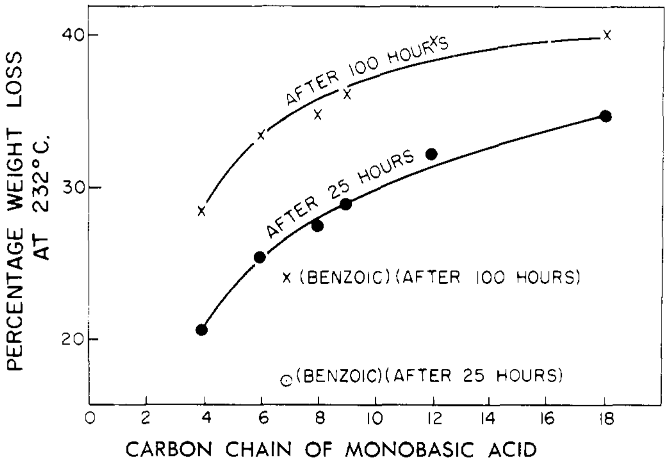


Figure 9. Effect of chain length of monobasic acid on percentage weight loss at 232° C.

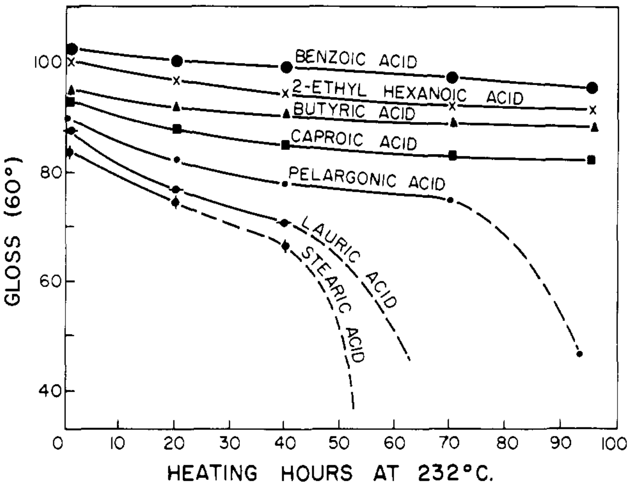


Figure 10. Effect of monobasic acids on gloss

Silicone-alkyds containing glycerol have been extensively studied by a number of investigators and by Hiles and others (*8*). The use of more highly functional polyols, such as pentaerythritol or dipentaerythritol, was avoided, because of the highly functional character of the silicone intermediates under study. Apart from their high functionality, which advances the gelation point and limits the copolymerization reaction to a lower percentage of conversion, such polyols are short-chained compounds which form with short-chained dibasic acids, such as the phthalic acids, very rigid network structures of inferior flexibility and compatibility. Improvement of these two properties was attempted. Considering all factors, trimethylolethane was the most satisfactory trihydric alcohol [see (*9*)].

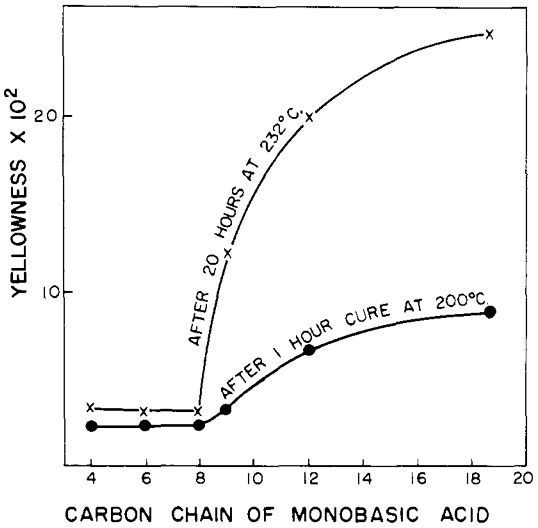


Figure 11. Effect of chain length of monobasic acid on yellowness

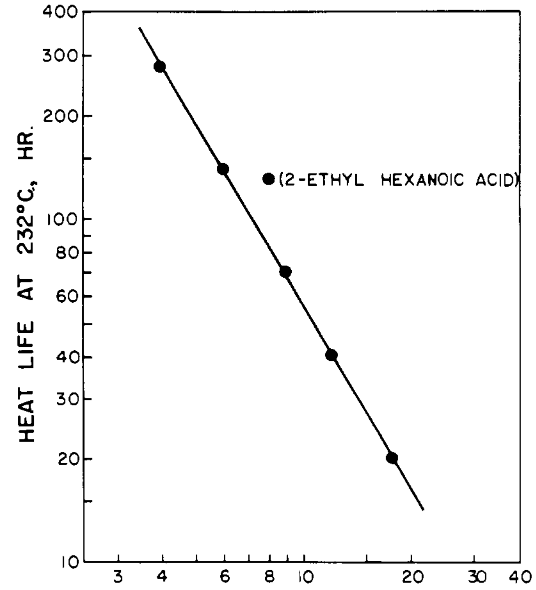


Figure 12. Effect of chain length of monobasic acid on heat life

Effect of the Dibasic Acid. To improve thermal stability, the phthalic acid isomers were also studied comparatively. Trimethylolethane and phenyl ethoxy polysiloxane were used, the latter at a concentration of 55%.

When processing alkyds containing isophthalic and terephthalic acids, it was necessary to modify the standard procedure used with phthalic anhydride. Stirring, carbon dioxide input, and temperature of reaction were adjusted to minimize the mechanical carry over of the volatile ingredients by the carbon dioxide and water evolved. Contrary to the recommendation of several investigators, the solvent method was preferable to the fusion method.

The rate of esterification of isophthalic acid was slow initially but the over-all rate was higher with isophthalic acid than with phthalic anhydride. In the copolymerization reaction, the rate of alcoholysis was also faster with isophthalic acid.

The compatibility of the silicone-alkyd varnishes made from the three isomeric acids decreased in the order phthalic, isophthalic, terephthalic, while thermal stabilities were in inverse order. The gloss and gloss retention of enamels made from comparable formulations of the phthalic acids were similar. During an exposure period of 100 hours at 232° C. (450° F.), only slight differences in gloss were noted among the three isomeric acids (Figure 14). Figure 15 shows that the phthalic acid used made no difference in heat life at 232° C. However, at 260° C. (500° F.), differentiation among the isomeric acids was greater. Enamels containing phthalic anhydride began to show signs of film failure within 50 hours upon heat exposure at 260° C. Terephthalic acid enamels showed a similar weakness at 288° C. (550° F.). Isophthalic acid enamels exhibited the best thermal stabilities and were able to stand in succession 100 hours each at 232°, 260°, and 288° C., while retaining film integrity and good color and gloss retentions.

The curing rates of the phthalic acid enamels increased in the order: phthalic anhydride, terephthalic acid, isophthalic acid. Hardness is a function of many variables; the type of monobasic acid used is a prominent factor.

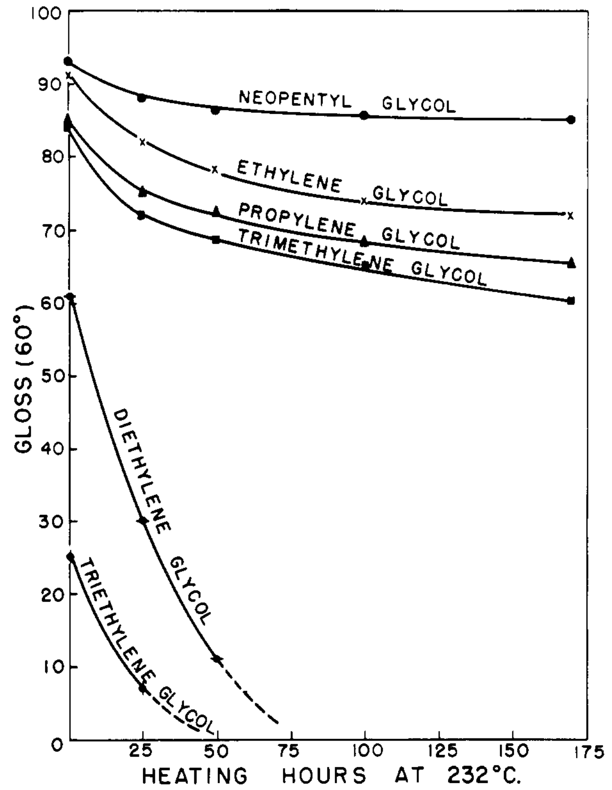


Figure 13. Gloss and gloss retention of different glycols

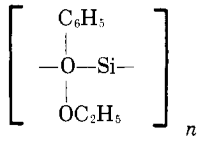
Table IV. Copolymer Properties Showing

	Composition and Processing					Varnish Properties			
Resin No.	% silicone	Kind of silicone[a]	% ethoxy	Dibasic acid	D/M	% solids	Acid no.	Color (Gardner)	% wt. loss 32 hr. at 232° C.
121	55	A	25	PA	1.6	74.4	7.0	2-3	28.7
123	55	B	92	PA	1.6	76.7	9.1	1-2	24.9
124	55	C	20	PA	1.6	74.9	5.7	2-3	37.2
125	55	D	20	PA	1.6	76.0	6.9	1-2	54.3
131	55	A	25	I PA	1.6	76.4	7.4	2-3	26.9
134	55	C	20	I PA	1.6	78.6	9.0	2-3	36.0
135	55	D	20	I PA	1.6	78.8	9.1	1-2	45.9
141	55	A	25	TPA	1.6	74.4	4.6	3-4	25.3
144	55	C	20	TPA	1.6	79.2	5.8	3-4	29.8
145	55	D	20	TPA	1.6	78.8	4.3	3-4	45.0

[a] Pigment to resin ratio was 2/3 for all samples.
[b] A = Phenyl ethoxy polysiloxane. B = Phenyl dimethyl polysiloxane.

There was no noticeable difference in alkali or hydrocarbon resistance among the formulations made with the three phthalic isomers. Enamels containing isophthalic acid showed a slight superiority in impact resistance and flexibility over those containing either phthalic anhydride or terephthalic acid.

Effect of the Silicone. Effect of the Ethoxy Content of the Silicone. The ethoxy content of an ethxy polysiloxane is a measure of its functionality and degree of polymerization. If phenyltrichlorosilane is treated with ethyl alcohol and any residual chloride hydrolyzed, the percentage ethoxy changes from 56% in the monomer, phenyltriethoxysilane [$C_6H_5Si(OC_2H_5)_3$], to 27% in the linear polymer, phenyl ethoxy polysiloxane.



$$\left[-O-\overset{C_6H_5}{\underset{OC_2H_5}{Si}}- \right]_n$$

If the ethoxy content of a silicone intermediate is below 27%, the polymer has undergone a certain degree of cross linking.

The effect of this variable on silicone-alkyd copolymers was studied with phenyl ethoxy polysiloxane intermediates of 10, 13.2 21.5, 25, and 39% ethoxy content in two series of experiments. Compatibility of the silicone and alkyd components decreased with decrease in the ethoxy content of the silicone, but storage life of the resins decreased with the increase in ethoxy content. The percentage weight loss increased with increase in the percentage ethoxy content. This may be attributed to a combination of several factors. First, the trans-esterification reaction that continues during the curing period proceeds to a greater extent in polymers whose chain length and configuration offer less steric hindrance to the penetration of the reactive groups. Second, cleavage of residual $\equiv Si-O-C_2H_5$ at the oxygen-carbon bond liberates diethyl ether and increases the length of the siloxane chain. This reaction does not increase the extent of copolymerization but instead causes greater brittleness in the resin film. Third, pyrolysis and sublimation of low-molecular-weight components occur.

The effect of ethoxy content was of secondary importance on the properties of the enamel film compared to the composition and stability of the alkyd component. However, when the decrease in ethoxy content limited the advance of the copolymerization reaction to an extent that it precluded good compatibility of the copolymer, its importance became major.

Taking an over-all picture of the ethoxy effect, the silicones with a medium ethoxy content of 15 to 25% gave no processing difficulties, good compatibility, superior thermal stability, high gloss, good color and color retention, and longer heat life. Evidently there is an optimum range of silicone chain-length and functionality which permits a more uniform distribution of the alkyd and silicone chains in the copolymer and results in a resin that combines best the properties of the two components.

Effect of Silicone Composition. Four silicone intermediates were copolymerized with comparable alkyd formulations containing the phthalic acids modified with benzoic acid. The first was an aryl silicone, phenyl ethoxy polysiloxane. Its percentage ethoxy was 25, average molecular weight, 1100, equivalent weight, 180, and R/Si ratio, 1. The second, Sylkyd 50, was a commercial alkyl-aryl methoxy polysiloxane made from methylphenyl and monophenyl substituted organosilicone. Its average molecular weight was 470, equivalent weight, 155, percentage methoxy, 20, and R/Si ratio, 1.66. The third was an alkyl-aryl silicone made by co-condensing 60 mole % of phenyltrichlorosilane with 40% dimethyldichlorosilane. Its average molecular weight was 2200, equivalent weight, 450, percentage ethoxy, 9.2, and and R/Si ratio of 1.4. The fourth was also a copolymer made by co-condensing 60 mole % of phenyltrichlorosilane, 20 mole % of dimethyldichlorosilane, and 20 mole % of diphenyldichlorosilane. Its average molecular weight was 700, equivalent weight, 225, percentage ethoxy, 20, and R/Si ratio, 1.4.

The results and processing characteristics are shown in Table IV. The toluene resistance after 50 hours was excellent for all resins listed. The main difficulties encountered in the copolymerization of the four different silicones were the result of incompatibilities. With monophenyl dimethyl polysiloxane of 9.2% ethoxy content, it was impossible to prepare homogeneous resins with any of the three phthalic isomers. Evidently the large molecular size of the silicone and the limited extent of the reaction prevented complete homogeneity in the final resins. Phenyl dimethyl diphenyl ethoxy polysiloxane presented no difficulty in preparing homogeneous resins with ortho- and isophthalic acids. With terephthalic acid, slight incompatibility of the copolymer produced inferior properties in the resins.

The homogeneous varnishes made from the three different silicones showed appreciable differences in percentage weight loss. Resins made from phenyl ethoxy polysiloxane had a lower percentage weight loss than either of the resins made from the aryl alkyl silicones, in spite of the fact that the percentage ethoxy in the former is higher than that in

Effects of Silicone Composition

Enamel Properties[a]															
Gloss								Hardness				Distensibility			
Hours at								Hours at							
200° C. 0.5	232° C. 26	232° C. 52	232° C. 75	260° C. 25	260° C. 50	288° C. 100	200° C. 0.5	232° C. 26	232° C. 52	232° C. 75	260° C. 50	1/2 inch mandrel	1/4 inch mandrel	Impact resist., in.-lb.
94	95	91	90	88	86	[c]	22	48	48	48	46	Pass	Fail	13
..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
97	92	88	88	80	72	55[d]	26	48	43	43	36	Pass	Pass	21
93	82	76	72	57	53	20	14	44	44	34	28	Pass	Pass	22
96	88	87	86	85	83	80	26	52	48	38	44	Pass	Fail	13
92	85	83	83	80	80	77	22	36	24	44	44	Pass	Pass	25
90	78	75	75	70	67	44	16	44	40	42	42	Pass	Pass	26
94	87	85	85	82	82	74	32	38	34	38	38	Pass	Fail	18
75	42	40	41	33	32	28	13	32	30	30	30	Pass	Fail	19
93	81	77	77	73	70	48	22	40	36	36	30	Pass	Pass	25

C = Phenyl diphenyl dimethyl ethoxy polysiloxane.
D = Sylkyd 50.

[c] Cracked.
[d] Slightly cracked.

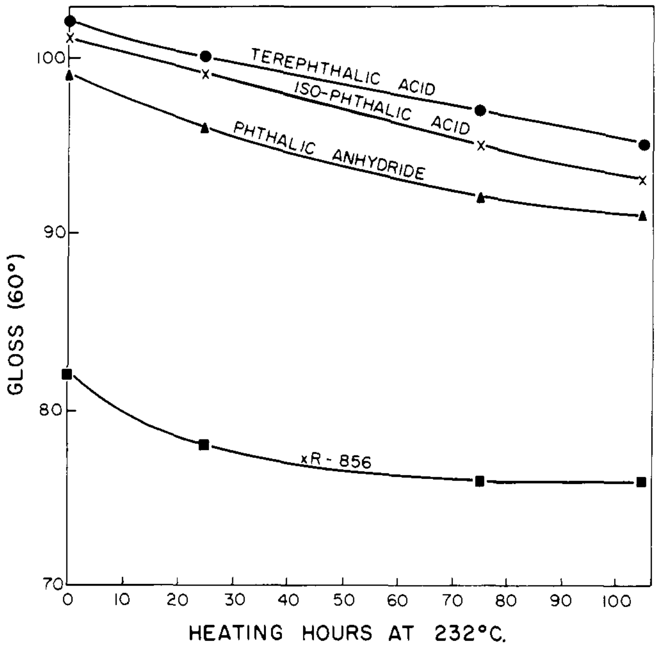


Figure 14. Gloss and gloss retention of phthalic acid isomers at 232° C.

the latter. The apparent anomaly may be attributed to the lower thermal stability of the methyl groups attached to the silicon atoms as compared with the phenyl groups. It may also be due to the molecular size of the silicone. The average molecular weight of the three silicones used in these comparative experiments were 1100, 700, and 470. It appears reasonable to find the percentage weight loss varying in the reverse order of the size of the silicone unit.

Enamels prepared from the three silicones showed a gradation in properties which was expected on the basis of their molecular structures and compositions. For example, enamels made from the pure aryl silicones had superior gloss and gloss retention as compared with enamels made from the alkyl-aryl. silicones. The differences were more distinct at 260° C. and above. At these temperatures, aryl silicones, which are more resistant to oxidation and decomposition, retained a high degree of gloss in enamels until their brittleness, which is one of their outstanding drawbacks, caused film failure by checking and cracking. On the other hand, the two alkyl aryl silicones, which are thermally less stable, suffered more serious decomposition which resulted in a more rapid decrease in gloss. Their flexibility, however, which is their chief advantage, permitted good film intregrity at gloss values as low as 20. The same trends in gloss and gloss retention were observed in the corresponding series of enamels made with isophthalic and terephthalic acids.

Very little differentiation was noticed in the alkali and solvent resistances of the various enamels examined in this series. All enamels showed no perceptible attack when immersed in toluene for 50 hours. Immersion in 3% sodium hydroxide solution for 96 hours at room temperature resulted in no film failure in any of the enamels, but the slight attack of the alkali caused a decrease in gloss accompanied by some chalking.

The results of this study are not in full agreement with some found by other investigators (*12, 13, 19*) who indicated that incorporation of alkyl and aryl silicones results in improvement of certain properties without sacrificing other desirable properties of the pure alkyl or aryl silicones. In this study, phenyl polysiloxane, a typical aryl silicone, was found to possess high gloss and good gloss retention in addition to superior thermal stability. Its chief drawback is a certain degree of brittleness which is responsible for its inferior flexibility, adhesion, and impact resistance. Phenyl diphenyl dimethyl polysiloxane, as well as phenyl phenyl methyl polysiloxane, are typical alkyl aryl silicone copolymers which demonstrated superior flexibility, impact resistance, and adhesion. These improved properties, however, were obtained at a considerable sacrifice in thermal stability, gloss, and gloss retention, which are extremely improtant properties in high-temperature surface coatings.

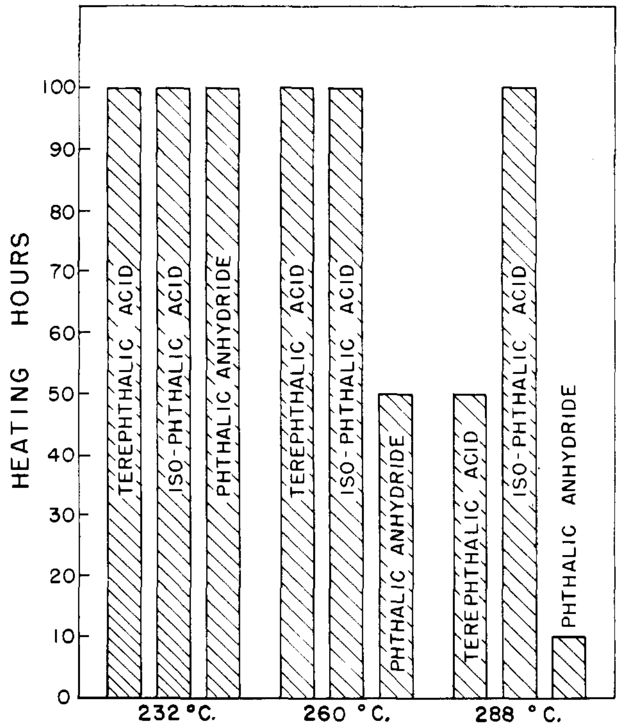


Figure 15. Heat life of phthalic acid isomers

SUMMARY

The limiting ratios of the silicone and alkyd components were determined in a system using phthalic anhydride, 2-ethylhexanoic acid, trimethylolethane, and phenyl ethoxy polysiloxane. Optimum compositions of copolymers were between 50 to 60% silicone and a dibasic to monobasic acid ratio close to two.

The monobasic acid was, thermally, the weakest constituent of the alkyd, and its chain length had a pronounced effect on the copolymer properties. While increasing chain length tended to increase the flexibility of the resin film, the greater decomposition of the longer-chain acids resulted in inferior gloss, color and color retention, and shorter heat life. The decomposition of the monobasic acids was an oxidation phenomenon.

In substituting various glycols for trimethylolethane, flexibility increased but thermal stability decreased with increase in glycol chain length. Although neopentyl glycol was the best of the glycols studied, the limited thermal stability of all the glycols precluded their use at service temperatures above 230° C.

The isomeric phthalic acids as constituents of the alkyd component were compared. Copolymers containing these acids showed slight differences in enamel properties at exposure temperatures of 230° C. or below. At 260° C., resins containing phthalic anhydride began to show signs of film failure; at 285° C., resins containing terephthalic acid showed similar failure. Resins containing isophthalic acid exhibited the best thermal stabilities and were able to withstand successively 100 hours each at 230°, 260°, and 285° C. while retaining film integrity, gloss above 80, good color, adhesion, alkali and solvent resistance, and a fair degree of flexibility.

Silicones with an ethoxy content of from 15 to 25% formed optimum copolymers with the alkyd resins—i.e., no processing difficulties, good compatibility, and superior thermal stabilities. Evidently there is an optimum range of silicone chain length and functionality which permits a more uniform distribution of the alkyd and silicone chains in the coploymer and results in a resin which best combines the properties of the two components.

Aryl silicones produce silicone-alkyd resins of superior thermal stability but of limited flexibility and adhesion. On the other hand, alkyl aryl silicones produce silicone-alkyd resins of superior flexibility, adhesion, and impact resistance. However, these properties were improved at a considerable sacrifice in thermal stability, gloss, and gloss retention, which are important properties in high-temperature surface coatings.

Some copolymers made during this investigation were superior with respect to maximum service temperature and at least equal in other properties to any known commercial product.

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LITERATURE CITED

(1) Brady, S. A., *Offic. Dig. Federation Paint & Varnish Production Clubs* **30**, 958 (1958).
(2) Brady, S. A., Johnson, J. C., Lyons, J. D., *Paint & Varnish Production* **48**, No. 1 (1958).
(3) Bunnell, R. H. (to Libbey-Owens-Ford Glass Co.), U. S. Patent **2,607,755** (Aug. 19, 1952).
(4) Earhart, K. A., *Ind. Eng. Chem.* **41**, 716 (1949).
(5) Emblem, H. G., others, *Plastics (London)* **12**, 137, 525 (1948).
(6) Glaser, M. A., *Ind. Eng. Chem.* **46**, 2334 (1954).
(7) Hatcher, D. B., Bunnell, R. H. (to Libbey-Owens-Ford Glass Co.), U. S. Patent **2,624,720** (Jan. 6, 1953).
(8) Hiles, C. R., Golding, B., Shreve, R. N., *Ind. Eng. Chem.* **47**, 1418 (1955).
(9) Hurd, C. D., Blunk, F. H., *J. Am. Chem. Soc.* **60**, 2419 (1938).
(10) Libbey-Owens-Ford Glass Co., Brit. Patent **694,716** (July 29, 1953).
(11) McLean, W. M. (to Dow Corning Corp.), U. S. Patent **2,687,398** (Aug. 24, 1954).
(12) Rochow, E. G. (to General Electric Co.), *Ibid.*, **2,258,222** (Oct. 7, 1941).
(13) *Ibid.*, **2,442,212** (May 25, 1948).
(14) Rose, K., *Materials & Methods* **41**, 2, 109-24 (1955).
(15) Smith, A. L., Brown, L. H., Tyler, L. J., Hunter, M. J., *Ind. Eng. Chem.* **49**, 1903 (1957).
(16) Sowa, F. J., U. S. Patent **2,605,243** (July 29, 1952).
(17) Speier, J. L., Jr. (to Dow Corning Corp.), *Ibid.*, **2,576,486** Nov. 27, 1951.
(18) Stebleton, L. P., Hedlund, R. C., *Paint Ind. Mag.* **69**, 10 14-16 (1954).
(19) Young, D. C., Kin, M., *Plastics and Resins* **5**, No. 12, 13 (1946).

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Air Oxidation of 12-Tricosanone

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THE OXIDATION of long-chain paraffins with gaseous mixtures containing molecular oxygen has been the subject of many articles and patents (*13-16*). Less is known about the course of oxidation of long aliphatic chains containing functional groups although such molecules, and ketones in particular, are important because they are the primary or secondary derivatives in paraffin oxidation (*4*) and give rise to the complex products found in industrial wax oxidation.

Ketone oxidations have been carried out on molecules containing relatively short alkyl chains at conditions usually much less severe than those used for wax oxidation (*2, 3, 8, 10*). To study the effect of oxygen on a long paraffin chain containing an isolated carbonyl group, 12-tricosanone was oxidized with air in the presence of manganese napthenate catalyst at 160° C. Various fractions of the product, obtained by chromatographic separation over silica gel, were examined for the presence of free and esterified mono- and dibasic acids. The product was also reduced with lithium aluminum hydride and analyzed for alcohols and glycols. The material blown overhead during the oxidation was distilled and found to contain acids, paraffins, and *n*-octanal.

EXPERIMENTAL

Oxidation of 12-Tricosanone. One hundred grams of the ketone (Armour & Co., recrystallized from methanol, melting point, 67-8° C.) and 2 ml. of 6% manganese napthenate in naptha were heated to 150° C. in a 250-ml. flask which was 2 inches in diameter and had a 1.5-inch dispersion disk at the bottom. Dry air was passed through the vigorously stirred melt at 2 cubic feet per hour and the temperature climbed to 160° C. in about 30 minutes, where it was maintained within 3°, for an additional 5 hours. The combined residues of three runs weighed 232.1 grams, while a total of 107.5 grams of overhead product was collected.

The overhead condensate was distilled through a 27-plate packed column, and the product distribution is given in Table I. The acid consituents were determined by a consideration of the boiling ranges and neutralization values while the hydrocarbons were identified by extraction of cuts with concentrated sulfuric acid and determination of the refractive index and specific gravity of each paraffin phase. Although 2, 4-dinitrophenylhydrazine reagent gave positive

Table I. Product Distribution in Overhead Condensate

Compound	Weight %
Light hydrocarbons	3.7
Water	51.7
Formic acid	4.5
Acetic acid	1.1
Propionic acid	1.1
Butyric acid	1.0
Octane	0.6
Nonane	4.3
Decane	12.8
Undecane	10.3
Octanal	Trace identified
Total	91.1