

SILICONE - ALKYD COPOLYMERS

BY

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ABSTRACT

The purpose of this investigation was to review and study the effects and interactions of various silicone-alkyd components on the properties of the copolymers, particularly as they bear on their thermal stability for high temperature surface coatings.

Alkyd resins were prepared by esterifying a dibasic acid and a monobasic acid with a poly-hydric alcohol in a quantity equivalent to the total acids and to the ethoxy content of the silicone at a temperature of 180 - 230°C, under an inert atmosphere, agitation, and azeotropic reflux in a solvent until the acid number had decreased to 10. A silicone was then copolymerized with the alkyd. The silicone-alkyds were evaluated as varnishes and enamels.

A statistically designed experiment was formulated using the three phthalic acid isomers in one level of concentration; benzoic acid in three levels of concentration; a silicone in three levels of composition and trimethylolethane in stoichiometric quantity to react with alkyd and silicone components.

Statistical analysis of variance showed:

(1) It made no difference on the stability of the copolymer what level of benzoic acid was used.

(2) Isophthalic acid produced copolymers which were the most stable of the isomeric dibasic acids used

at temperatures of 250°C and above where differentiation became significant.

(3) Of the three silicone intermediates studied the aryl silicone, phenyl ethoxy polysiloxane (25% ethoxy), and the alkyl-aryl silicone, phenyl (60) dimethyl (20) diphenyl (20), ethoxy polysiloxane, showed no significant differentiation at exposure temperatures below 250°C. At temperatures above 250°C the aryl silicone showed superior thermal stability, good gloss and color retention. However, the alkyl-aryl silicone which retained adhesion and flexibility at temperatures above 250°C, suffered a significant decrease in gloss and increase in yellowness which are correlated with more serious manifestations of molecular degradation and decomposition. Sylkyd-50 was by far the least stable of the three.

(4) Two factor interactions were not significant in all copolymers at exposure temperatures of 225°C and below. At higher temperatures two factor interactions became quite significant. DS interactions were significant in gloss, yellowness and percentage weight loss. MS interactions were manifested in gloss and MD interactions in percentage weight loss measurements. Evidently at such temperatures the various silicone-alkyd components are not independent variables, and the properties of the copolymers are significantly affected by the degradations and possible molecular rearrangements

involving at least two components. It was not possible to analyze three factor interactions in this study.

The effect of various polyols on silicone-alkyd copolymers was explored by employing 1, 2, 6-hexanetriol, trimethylol propane, trimethylol ethane, pentaerythritol, alone or mixed with neopentyl glycol and 1, 5-pentane diol. It was found:

(1) That of the triols TME produced resins of overall superior properties. Resins containing 1,2, 6-hexanetriol showed lower extent of copolymerization and lowest thermal stability.

(2) Enamels containing mixed polyols showed intermediate retention of gloss and yellowness.

(3) Mixed formulations of TME and neopentyl glycol showed superior thermal stability to those of TME, and 1, 5-pentane-diol.

(4) Enamels containing trimethylol propane showed up to 250°C intermediate properties.

(5) The only enamels which were able to stand a temperature of 275°C were those that contained TME and pentaerythritol with neopentyl glycol.

A comparative study of the monobasic acid effect on TME and trimethylol propane was performed. Of the mono-basic acids used benzoic acid, p-tertiary butyl benzoic acid, caproic acid and trichloro-acetic were employed.

It was found that enamel stability was decreased in the order benzoic acids, p-tertiary butyl benzoic acid, and caproic acid.

In processing alkyds containing strong acids such as trichloro-acetic acid, and p-nitrobenzoic acid, side reactions, other than esterification, resulted in excessive decomposition and the liberation of a yellow distillate which readily decolorized KMnO_4 but did not add bromine. A mechanism involving a Whitmore rearrangement has been proposed to explain this observation.

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INTRODUCTION

I. SURVEY OF THE LITERATURE

Silicone-alkyds had their first appearance in the literature in 1947.

Bowman and Evans (1) condensed modified alkyd resins with an organosilicol in a solvent process and obtained a heat-resistant surface coating. Patterson (2, 3, 4) reported in a number of articles that the presence of silicone resin exerts a strong protective action on the alkyd, making the copolymers intermediate in heat resistance between pure silicones and alkyd-melamines.

Kress and Hoppers (5) reviewed in 1952 the properties and formulations of silicone-alkyd enamels. In the same year, Pattison (6) described the use of silicone-alkyd resins for heat, water, chemical and weather resistance.

In 1954 and 1955 a number of articles were published by Hedlund (7), Stebleton and Hedlund (8), Hoffmeister (9), Rose (10), and Hiles, Shreve and Golding (11) reviewing the recent developments in the chemistry, properties and application of modified silicone copolymers.

The patent literature on silicone-alkyds is richer than the published literature. This is logical and is expected since silicone-alkyds were developed in industrial research centers.

Bowman and Evans (1) were issued the first patent in the subject. In 1951, British Thompson-Houston Co. Ltd. (12) registered a patent covering the preparation of oil-modified alkyd resins with organopolysiloxanes.

During 1952 a large number of patent claims on silicone alkyds were registered. The patents that were issued to Goodwin and Hunter (13), Hunter and Rauner (14), Doyle and Nelson (15), Goodwin and Hunter (13), and many others (16) claimed advantages of one sort or another in the processing, properties, applications and cost of silicone-alkyd resins.

During 1953 and 1954 fewer patents were issued on the subject (17). Silicone research began to show some activity in new copolymers. Mclean (18) was issued a patent on silicone-epoxy copolymers. Passino and Rubin patented heat resistant polymers of fluoro-alkyl silicon derivatives such as $(CF_3)_2 SiCl_2$ and $(C_3F_7)_2 SiCl_2$.

In 1956 Kress (19) was issued a patent on coating compositions which have superior weather and chemical resistance, added to good curability and compatability in aliphatic hydro-carbon solvents.

The present investigation was suggested by the results obtained in a previous work done at Purdue University (20). Since this study is more or less a continuation on this previous work, its findings are briefly summarized:-

(1) In a system using phthalic anhydride, 2-ethyl hexoic

acid, trimethylol ethane (TME) and phenyl ethoxypoly-siloxane, optimum compositions of silicone-alkyd copolymers contained between 50 - 60% silicone and a di-basic to monobasic acid ratio of 2:1 equivalents.

(2) Of the alkyd components the monobasic acid was thermally the weakest, and its chain length had a pronounced effect on the thermal stability and flexibility of the copolymers.

(3) In substituting various glycols for trimethylol ethane flexibility was increased, but thermal stability was found to decrease with increase in chain length. Neopentyl glycol was found to be the best of the glycols studied.

(4) Comparative studies using the isomeric phthalic acids showed that isophthalic acid produced silicone-alkyd copolymers which had overall superior properties for high temperature surface coatings.

(5) Silicone intermediates with 15 to 25% ethoxy content gave optimum copolymers with alkyd resins. Aryl silicones produced silicone-alkyd resins of superior thermal stability, but of limited flexibility and adhesion. On the other hand, alkyl-aryl silicones produced copolymers of improved flexibility and adhesion but at the expense of a decrease in thermal stability.

The aim of the present study was: first, to review some of the good formulations, obtained by this former

study, in a statistically designed experiment, with the intention of getting some further insight into the effects and interactions of the various silicone-alkyd components, particularly during the degradation period at high temperatures.

Second, to explore a number of avenues that were recommended for further study. This included: (1) reducing the functionality of the polyol by mixing triols and tetrols with diols, such as neopentyl glycol.

(2) Using longer chain triols such as 1, 3, 6 - hexanetriol or 1, 3, 5 pentanetriol, which are expected to have less steric effects on copolymerization and may help to increase the flexibility of the copolymers.

(3) Studying the effect of substituting trimethylol propane, a new comer to commercial production, for trimethylol ethane. The former has a longer alkyl group and may increase the compatibility of the copolymers. (4) Studying the effect of stronger aliphatic acids such as dichloro and trichloro-acetic acid as well as substituted aromatic acid such as P-nitrobenzoic acid.

THEORETICAL

Alkyds have been defined as polymeric condensation products of polyhydric alcohols and polybasic acids.

Theoretically any bifunctional or polyfunctional alcohol

and acid might be used in the making of polyesters provided cyclization does not occur.

Bifunctional acids and alcohols produce linear thermoplastic resins, which are relatively soft, flexible and may possess film-forming or fibrous characteristics. If the functionality of either the acid or the alcohol is greater than two then three dimensional polymerization becomes possible and the products are thermo-setting resins which are in general, hard, brittle and of limited compatibility with organic solvents. By varying the functionality of either acid or alcohol we can get products exhibiting all intermediate properties.

ALKYDS.

Alkyd reactions are usually carried out by either mass or solution polymerization. Mechanical difficulties, inefficient control of heat and appreciable losses incurred in mass polymerization, render solution polymerization preferable. Although the solvent decreases the reaction rate and the average molecular weight of the alkyd resin, it has the advantages of giving a more uniform molecular weight distribution, better control of the reaction, and no unaccounted losses in the alkyd system.

SILICONES.

Silicones are hydrolysis products of alkyl or

aryl silicon halides.

The protective effect of the siloxane chain on the organic group is thought to be due to the high ionic character and polarity of the siloxane bonds.

Of the organic substituents phenyl and methyl groups confer the best heat resistance. Increase in the alkyl or aryl group diminishes the protective effect of the siloxane bond, and hence, decreases the thermal stability of the silicone.

Copolymerization between alkyds and silicones is essentially a co-condensation reaction between the functional groups of both reactants. In alkyds the functional groups are the hydroxyl and carboxyl groups, while in the silicone intermediates the alkoxy groups.

EQUIPMENT

The alkyds were prepared in a 500 mls. round bottom flask with four ground glass necks. To these were fitted a filling tube, an inert gas delivery tube (CO_2), a thermometer, a collapsible double bladed stainless steel^{stirrer} sealed with an adjustable graphite packing gland and driven by a variable-speed motor, and a reflux condenser with a Stark and Dean trap. Heating of the reaction flask was accomplished by using an electrically heated mantle, controlled by a variac auto-transformer. A flow-meter was inserted in the inert gas line to measure the rate of input of CO_2 . All this set-up used for the preparation of alkyds is illustrated in figure 1.

For copolymerization, the reflux condenser and its Stark and Dean trap were disconnected and a fractionating column inserted in its place. The latter was 55cms. long and packed to a height of 35 cms. with glass helices and glass heads. To the top of the column a condenser was added. The alcohol, liberated from the alcoholysis reaction, was collected in a graduated cylinder attached to the condenser thru an adapter. Photograph 2. Figure 2.

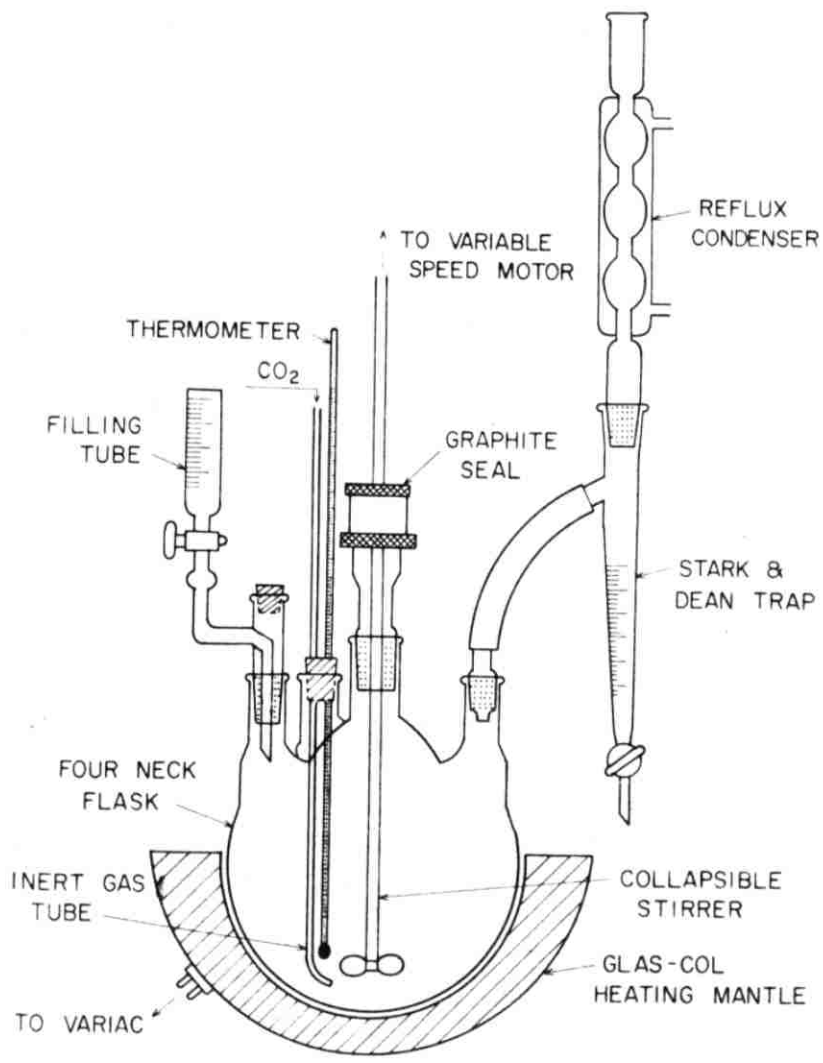


FIGURE 1
 APPARATUS FOR PREPARATION OF RESINS

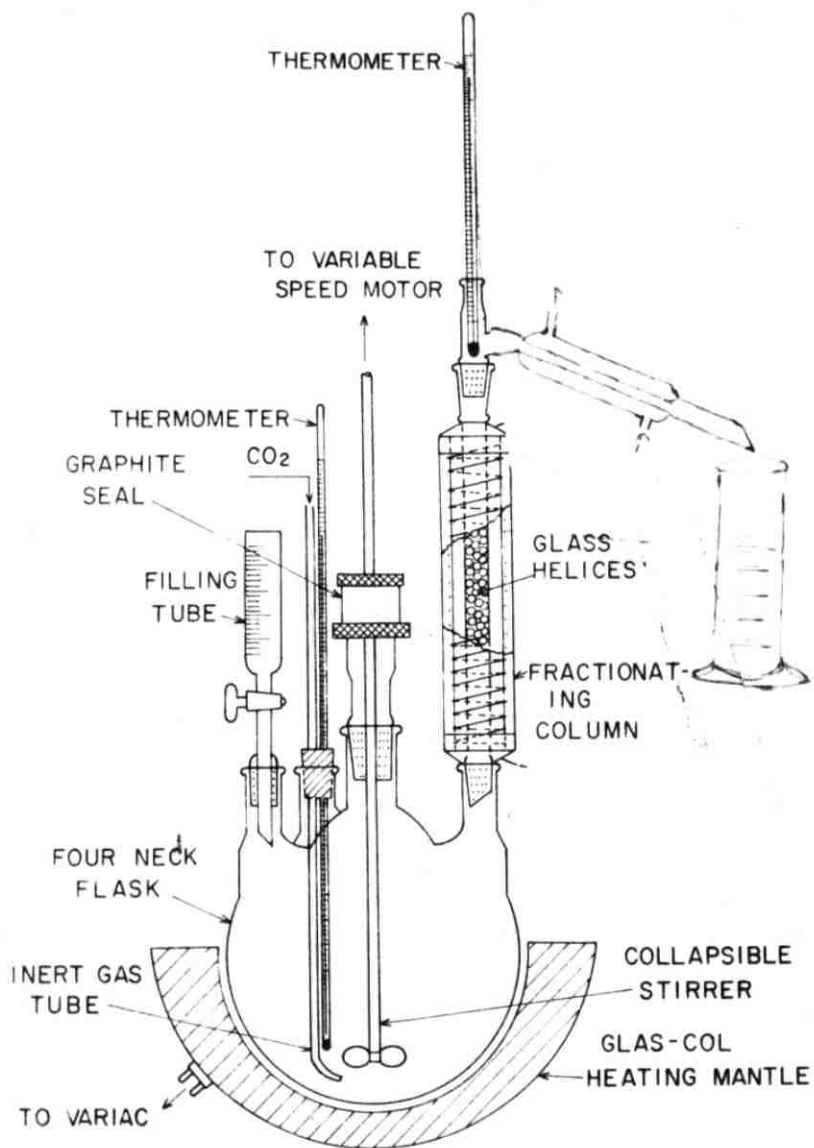


Figure 2

Apparatus for Copolymerization

PROCEDURE

The desired quantities of polyol, dibasic and mono-basic acids were added into the reaction flask. Then thru the filling tube, the selected solvent was added in an amount equal to 10 - 15% of the weight of the reactants. The mixture was heated at a fast rate to a steady reflux, which was normally between 180 - 220° C.

Simultaneously, the stirrer was started at a moderate rate to prevent local over-heating and 100 - 200 cc / min. of CO₂ were allowed to bubble thru the mixture. Later, once the whole batch melted, the stirring rate was adjusted to 600 - 800 r.p.m.

The produced water was collected in the Stark and Dean trap, and the reaction temperature was allowed to increase slowly to 230°C. This was done by bleeding a small amount of solvent thru the Stark and Dean trap.

When the amount of water was one or .5 mls. off the theoretical, a sample of resin was withdrawn and titrated against a standard alcoholic solution of KOH to determine the acid number. When the acid number fell below 10, the heating mantle was dropped and the resin allowed to cool to below 170°C. In the meantime the reflux condenser and Stark and Dean trap were disconnected and replaced by the fractionating column shown in fig. 2. The desired amount of silicone was added to the alkyd resin. An additional quantity of diisobutyl ketone equal to 10 -

20% of the weight of the reactants, was added. Stirring was resumed at 800 - 900 r.p.m. and heating adjusted to 185 - 190°C. Thus the thermometer at the top of the reflux condenser showed a temperature a little lower to that of the boiling point of the specific alcohol liberated.

At first the reaction mass was incompatible. As the reaction proceeded the mass became clearer until, within 30 -40 minutes, it became homogeneous. The reaction was continued until the resin became almost a stagnant mass and no cavitation around the stirrer was noticeable. The reaction was stopped by lowering the heating mantle and adding enough mixture of butyl-acetate and diisobutyl ketone (1:1) to reduce the copolymer mass to 60 - 70% total solids.

In the preparation of enamels the rutile form of titanium dioxide was exclusively used. To prepare the enamel 125 gms. of TiO_2 were placed in a bowl fitted to a mixer of variable speed. When the grind became completely wetted the speed of stirring was increased and varnish was slowly added until a smooth paste was formed. This paste was then passed twice thru a three-roll mill. The well ground paste was weighed and the additional amount of varnish needed to give a resin to pigment ratio of 3:2, was added. Then the enamel was thinned with solvent consisting of turpentine , diisobutyl-ketone & butyl -

acetate (in the proportions 1:1:2) to a viscosity of 25 seconds as measured by Ford Cup No. 4. The thinner was incorporated gradually so that no separation occurred. Then the enamel was centrifuged at 2000 r.p.m. in order to separate any oversized particles, bottled and labeled.

The enamel was then tested by spraying on :

(1) Steel panels of 0.4 mm. thickness and 8×12 cm². The thickness of the enamel film was $.9 \pm .1$ mil. throughout the various tests. These steel substrates were degreased in toluene using steel wool for roughening the surface followed by a final rinse in clean toluene and the panel allowed to air-dry. Before enamel application the clean panels were heated for about 15 minutes at 200°C. This treatment was suggested to improve the adhesion of the enamel film. (2) Glass panels of 8×12 cm².

Gloss was measured by a Photovolt 60° gloss meter, while yellowness was measured by the same gloss meter using tristimulus filters and applying the equation:-

$$Y = \frac{A - B}{G}$$

where A amber, B blue and G green contributions respectively. Finally hardness was measured by a Sward Rocker.

EXPERIMENTAL

A. Effect of Silicone and Alkyd Constituents on Copolymer Properties.

The effect of each of the silicone and alkyd components on copolymer properties was studied previously (20) by the conventional method in which all variables were fixed except the one under study. It is thought that a further insight into this matter could be achieved by a statistical approach in which the desired variables are allowed to change simultaneously. Analysis of the results may give a clearer picture of the interactions and overall effects of the various components.

A large number of ingredients are industrially used in preparing alkyd and silicone resins. The components selected in this study were taken from formulations (20) which demonstrated superior properties for high temperature surface coatings.

An experiment was designed in which the dibasic acid (D) was studied at one level of concentration and three levels of composition; the monobasic acid (M), at one level of composition and three levels of concentration, the silicone (S) at three levels of composition and one level of concentration. The latter was fixed at 55% of the weight of the copolymer. Finally, the polyol (P) was fixed at one level of composition and its concentration was stoichiometrically determined by the other components.

This statistically designed problem which consisted of 27 experiments is outlined below:

TABLE I.

1	$M_1D_1S_1$	13	$M_2D_1S_1$	25	$M_3D_1S_1$
3	$M_1D_1S_2$	15	$M_2D_1S_2$	27	$M_3D_1S_2$
4	$M_1D_1S_3$	16	$M_2D_1S_3$	28	$M_3D_1S_3$
5	$M_1D_2S_1$	17	$M_2D_2S_1$	29	$M_3D_2S_1$
7	$M_1D_2S_2$	19	$M_2D_2S_2$	31	$M_3D_2S_2$
8	$M_1D_2S_3$	20	$M_2D_2S_3$	32	$M_3D_2S_3$
9	$M_1D_3S_1$	21	$M_2D_3S_1$	33	$M_3D_3S_1$
11	$M_1D_3S_2$	23	$M_2D_3S_2$	35	$M_3D_3S_2$
12	$M_1D_3S_3$	24	$M_2D_3S_3$	36	$M_3D_3S_3$

where:

M_1 1 equivalent of Benzoic Acid.

M_2 1.25 equivalent of Benzoic Acid.

M_3 1.5 equivalent of Benzoic Acid.

D_1 2 equivalents of Phthalic anhydride.

D_2 2 equivalents of Isophthalic acid.

D_3 2 equivalents of Terephthalic acid.

S_1 phenyl ethoxy polysiloxane (25% ethoxy).

S_2 phenyl (60) dimethyl (20) diphenyl (20) ethoxy polysiloxane. (20% ethoxy).

S_3 trimethoxy - triphenyl - dimethyl - trisiloxane. (20% methoxy).

A sample calculation will illustrate how the silicone and polyol components were calculated in the various formulations:

<u>Experiment</u> <u>I.</u>	No. of equivts.	equivlt. weight.	total weight.
M ₁ Benzoic acid.	1	122	122
D ₁ Phthalic anhydride.	2	74	148
Polyol Trimethylol ethane.	3	40	<u>120</u>
			390
			- 36
			<u>354 gms.</u>

less of two moles of water liberated

weight of alkyd component - - - - - 354 gms.

S₁ weight of S₁ in product $354 \frac{55}{45}$ - - - - - 433 gms.

S₁ has an equivalent weight of - - - - - 180 gms.

Equivalents of S₁ needed $\frac{433}{180} = 2.41$

hence total amount of TME needed $3 \times 2.41 = 5.41$ equivalents $5.41 \times 40 =$ 216.4 gms.

Hence experiment 1 (M₁D₁S₁) is formulated as follows:

Reactants.	equivts.	equivt. weight.	total weight.
M ₁ Benzoic acid	1	122	122
D ₁ Phthalic anhydride	2	74	148
S ₁ Silicone	2.41	180	433
Polyol TME	5.41	40	216.5

All copolymers were tested as varnishes and as enamels. Percentage weight loss, gloss, hardness, adhesion and heat life were the five main criteria on which

the copolymers were analyzed.

An illustration of a silicone alkyd copolymer, as it is believed to be synthesized in the forthcoming experimental work, is given below. The silicone intermediate is phenyl dimethyl diphenyl ethoxy polysiloxane. Its high functionality is shown by the number of ethoxy groups on a sample molecule. The polyol is trimethylol ethane, the dibasic acid phthalic anhydride, and the monobasic acid benzoic acid.

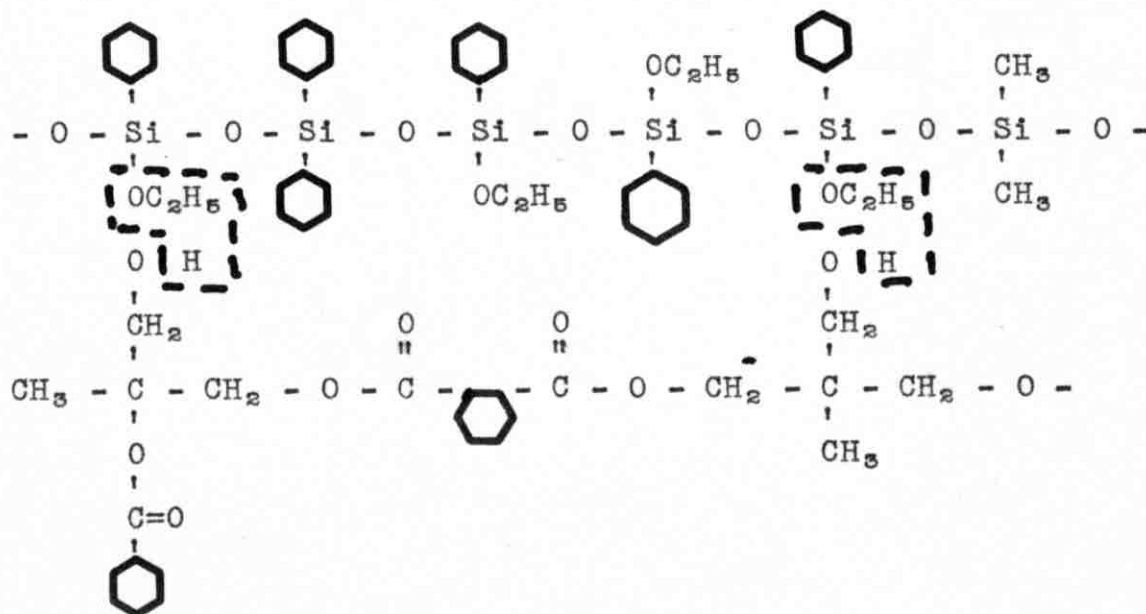


TABLE II

GLOSS.

YELLOWNESS

No.	Silic.	No. D.	D/M	Alcohol		A.N.	Initial	GLOSS.			YELLOWNESS						
				cc./equivt.	% solids			25 hrs. 225° C.	50 hrs. 225° C.	25 hrs. 250° C.	50 hrs. 250° C.	25 hrs. 275° C.	25 hrs. 225° C.	50 hrs. 225° C.	25 hrs. 250° C.	50 hrs. 250° C.	25 hrs. 275° C.
1	S ₁	P.A.	2/1	27 E	65.0	.15	94	70	58	---	---	---	.058	.058	---	---	---
3	S ₂	P.A.	2/1	35 E	61.0	10	100	83	78	66	56	---	.023	.023	.049	.072	---
4	S ₃	P.A.	2/1	32 M	61.7	5	87	80	69	52	43	---	.012	.012	.020	.024	---
5	S ₁	I.A.	2/1	28 E	54.6	3.9	95	93	92	80	74	---	0	0	.090	.115	---
7	S ₂	I.A.	2/1	29 E	61.7	4.3	96	87	88	81	76	---	0	0	.050	.095	---
8	S ₃	I.A.	2/1	31 M	63.9	10	99	58	55	39	39	---	.080	.111	.185	.185	---
9	S ₁	T.A.	2/1	24 E	61.3	8.7	98	67	66	56	50	---	.115	.115	.197	.197	---
11	S ₂	T.A.	2/1	31 E	63.1	9.5	100	84	80	59	56	42	.036	.037	.106	.106	.153
12	S ₃	T.A.	2/1	29 M	60.7	6.7	98	82	74	60	54	47	.052	.109	.195	.185	.213
13	S ₁	P.A.	2/1.25	28 E	63.3	1.2	98	47	40	23	---	---	.023	.023	.091	---	---
15	S ₂	P.A.	2/1.25	37 E	60.7	6.7	96	81	78	61	55	---	.024	.024	.062	.062	---
16	S ₃	P.A.	2/1.25	32 M	63.2	3.2	97	51	42	27	25	---	0	0	.049	.049	---
17	S ₁	I.A.	2/1.25	44 E	62.1	3.4	98	88	88	78	79	74	0	0	.049	.049	.088
19	S ₂	I.A.	2/1.25	36 E	61.6	5.4	99	93	87	75	78	72	.023	.023	.042	.042	.104
20	S ₃	I.A.	2/1.25	34 M	61.3	5.4	97	95	90	83	80	56	0	0	.037	.037	.147
21	S ₁	T.A.	2/1.25	27 E	65.5	9.4	100	93	91	81	81	69	.025	.025	.093	.113	.118
23	S ₂	T.A.	2/1.25	31 E	64.2	8.1	98	85	82	62	63	51	.024	.024	.150	.175	.167
24	S ₃	T.A.	2/1.25	26 M	63.4	8.7	92	69	65	48	45	35	.165	.165	.204	.218	.203
25	S ₁	P.A.	2/1.50	33 E	63.8	9.0	96	64	58	41	---	---	.048	.050	.087	---	---
27	S ₂	P.A.	2/1.50	42 E	62.5	5.5	88	73	67	52	46	---	.024	.024	.062	.099	---
28	S ₃	P.A.	2/1.50	35 M	63.0	5.2	93	62	53	35	35	---	0	0	.036	.036	---
29	S ₁	P.A.	2/1.50	31 E	62.3	9.3	98	94	93	83	83	---	0	0	.053	.078	---
31	S ₂	I.A.	2/1.50	38 E	62.0	4.0	98	84	89	75	75	60	.011	.012	.053	.060	.118
32	S ₃	I.A.	2/1.50	34 M	63.0	1.9	88	86	80	52	47	---	.035	.041	.105	.138	---
33	S ₁	T.A.	2/1.50	27 E	58.3	1.0	100	98	98	84	88	79	.048	.050	.086	.086	.105
35	S ₂	T.A.	2/1.50	35 E	63.2	3.0	95	71	70	49	46	44	.035	.038	.111	.126	---
36	S ₃	T.A.	2/1.50	30 M	62.6	8.8	95	83	79	52	50	48	.061	.125	.189	.189	---

All enamels had an initial yellowness of zero.

TABLE III.

No. of varnish.	Wt. percent loss after 20 hrs. of exposure at 250°C.	Wt. percent loss after 40 hrs. of exposure at 250°C.	Wt. percent loss after 90 hrs. of exposure at 250°C.
1	35.1	38.8	44.8
3	44.8	47.7	51.2
4	58.0	61.1	63.3
5	29.8	34.4	41.2
7	42.6	48.4	53.5
8	51.6	58.0	63.1
9	29.4	35.7	40.8
11	40.4	47.0	53.5
12	46.5	54.2	63.9
13	37.2	40.6	44.3
15	46.1	49.4	51.4
16	57.7	61.6	63.6
17	29.4	35.4	37.7
19	38.8	45.9	51.7
20	49.4	55.5	62.8
21	24.6	31.5	40.3
23	38.9	44.7	52.8
24	48.8	55.7	64.0
25	34.8	38.4	42.9
27	47.7	50.7	53.2
28	58.8	62.0	63.9
29	33.5	37.6	42.1
31	42.1	49.3	54.1
32	52.6	60.2	65.2
33	24.6	31.9	37.4
35	40.2	45.9	52.3
36	49.4	55.9	63.5

Percentage Weight Loss Analyses.

Table II and III give a summary of the resin compositions and their properties as evaluated by the tests conducted on the varnishes and enamels made therefrom. The percentage weight loss of resins heated at 250°C. for definite time intervals, was used as a comparative measure of their relative heat stabilities.

Table IV shows clearly that after 20 hours of heat exposure at 250°C the monobasic acid in its three levels of concentration was not significant. i.e., it made no difference on the stability of the resins as measured by their percentage weight loss whether M_1 , M_2 or M_3 were used in their preparation. On the other hand, table IV shows that the D and S variables were both significant with the latter being to a more appreciable extent. Evidently, silicone-alkyd resins made from isophthalic and terephthalic acids (D_2 and D_3) and phenyl-ethoxy-polysiloxane (S_1) showed better thermal stability than other comparative resins. However, at this stage of heat exposure no two factor interactions are significant.

Table V shows that after 40 hours of heat exposure the value of the dibasic acid (D) is still significant, while the silicone (S) becomes the factor of primary significance in determining heat stability. Two factor interactions are still insignificant.

After 90 hours of heat exposure, table VI reveals that the silicone is still the one factor variable of predominant significance, but two factor interactions start to assume significance. Such results would indicate that while the aryl silicone (S_1) is still the most stable of the three silicones, the properties of the resins are significantly affected by the degradations and possible molecular rearrangements involving the dibasic and monobasic acids.

TABLE IV.

Analysis of variance : Loss after 20 hrs. of exposure at
250°C. (Percentage weight).

S.V. source of variance	D.F. degrees of freedom	S.S. sum of squares	M.S. mean square	observed F.	F 5%
M	2	9.17	4.58	-----	4.46
D	2	342.96	171.48	-----	4.46
S	2	2102.19	1051.09	-----	4.46
MD	4	14.86	7.43	.58	3.84
MS	4	4.15	2.08	.16	3.84
DS	4	16.07	8.03	.63	3.84
MDS	8	25.59	12.79	-----	-----
Total	26	2514.99			

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	9.17	4.59	1.51	3.49
D	2	342.96	171.48	56.53 *	3.49
S	2	2102.19	1051.10	346.50 *	3.49
Error	20	60.67	3.03		
Total	26	2514.99			

TABLE V.

Analysis of variance : Percentage Wt. loss after 40 hrs.
of exposure at 250°C.

S.V.	D.F.	S.S	M.S.	F.	F 5%
M	2	7.52	3.76	---	4.46
D	2	127.15	63.58	---	4.46
S	2	2221.67	1110.84	---	4.46
MD	4	17.90	4.47	3.00	3.84
MS	4	8.11	2.03	1.36	3.84
DS	4	8.97	2.24	1.50	3.84
MDS	8	11.90	1.49		
Total	26	2403.22			

S.V.	D.F.	S.S.	M.S.	Observed F.	F 5%
M	2	7.52	3.76	1.60	3.49
D	2	127.15	63.58	27.12 *	3.49
S	2	2221.67	1110.84	473.906 *	3.49
Error	20	46.88	2.34		
Total	26	2403.22			

TABLE VI

Analysis of variance : Percentage loss after 90 hrs of exposure at 250°C.

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	3.02	1.51	.378	6.94
D	2	6.01	3.00	-----	
S	2	2262.53	1131.24	147.30 *	6.94
MD	4	16.02	4.00	5.71 *	3.84
DS	4	30.72	7.68	10.97 *	3.84
MS	4	4.84	1.21	1.73	3.84
MDS	8	5.62	.70		
Total	26	2328.77			

Gloss Analysis

Gloss, color, retention, and a long heat life at the expected service temperatures are some of the most important properties that high temperature enamels must have to be of value in surface coatings.

Table II shows that all enamels after curing had superior gloss. After 25 hours of heat exposure at 225°C, Table VII indicates that no significant differentiation was demonstrated by the M and S variables and only the D component was responsible for a significant change in the gloss of the enamels. Reference to Table II reveals that of the dibasic acids, isophthalic acid gave enamels of superior gloss to those of the ortho and para isomers.

After 50 hours of heat treatment at 225°C, Table VIII indicates that D is still the one factor variable that is significant at 5% and 1% levels, while S starts to assume significance at the 5% level. Evidently the silicone intermediate Sylkyd - 50 (S₃) which has lower average molecular weight than either of the two other silicone intermediates (S₁ and S₂) and a higher R/S₁ ratio, (R/S 1.66 for S₃ compared to an R/S₁ ratio of 1 for S₁ and S₂), is more sensitive to heat treatment and consequently incurs more serious decomposition which is demonstrated by an appreciable decrease in gloss of the enamels made therefrom. It is worth noting that at this stage of polymer degradation no significant differentiation

in gloss is demonstrated by S_1 and S_2 nor by any two factor interactions.

On exposing enamels to more drastic heat treatment, i.e., 25 hrs. at 250°C, degradation starts to show its effect on the more stable constituents. Table IX shows that M and ^Dvariables are no more independently significant and two factor interactions particularly MS and DS become of significance.

Analysis of variance at higher temperatures and longer heat treatment was impossible, as a large number of the enamels were cracked or peeled off from the panels, making a gloss measurement meaningless.

TABLE VII

Analysis of variance : Gloss at 225°C after 25 hrs of
exposure .

S.V.	D.F.	S.S.	M.S.	Observed F.	F 5%
M	2	10.67	5.34	----	4.46
D	2	1616.67	808.34	----	4.46
S	2	310.17	155.08	----	4.46
MD	4	836.66	206.67	1.44	3.84
MS	4	405.83	101.46	.707	3.84
DS	4	583.16	145.79	1.016	3.84
MDS	8	1147.51	143.44		
Total	26	4900.67	1566.11		

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	10.67	5.337	.036	3.49
D	2	1616.67	808.335	5.46 *	3.49
S	2	310.17	155.085	1.047	3.49
Error	20	2963.16	148.158		
Total	26				

TABLE VIII

Analysis of variance : Gloss at 225°C after 50 hrs of
exposure.

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	67.56	33.78	-----	4.46
D	2	2917.56	1458.78	-----	4.46
S	2	696.23	348.11	-----	4.46
MD	4	622.22	155.56	1.14	3.84
MS	4	315.21	78.80	.58	3.84
DS	4	793.55	198.39	1.45	3.84
MDS	8	1096.34	137.04		
Total	26	6508.67			

S.V.	D.F.	S.S	M.S.	F.	F 5%
M	2	67.56	33.78	.390	3.49
D	2	2917.56	1458.78	16.855*	3.49
S	2	696.23	348.16	4.02	3.49
Error	20	1730.98	865.5		

TABLE IX

Analysis of variance : Gloss at 250°C after 25 hrs of
exposure.

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	21.41	10.70	.07	6.94
D	2	3934.30	1967.15	2.53	6.94
S	2	1122.08	561.04		
MD	4	408.37	102.09	2.93	3.84
MS	4	605.26	151.31	4.35 ^x	3.84
DS	4	3112.37	778.09	22.37 ^x	3.84
MDS	8	278.29	34.79		
Total	26	9482.08	364.70		

Analysis of Yellowness

Yellowness in a white enamel is in general a sign of film decomposition and is usually correlated with a decrease in gloss, flexibility and adhesion. Increase in yellowness with heat and time is a sign of poor color retention and is considered an undesirable service characteristic of the enamel.

Table II shows that all enamels after curing had zero yellowness and a high degree of gloss. After 25 hours of heat exposure at 225°C Table X shows that of the one factor variables, D was significant. Resins containing isophthalic acid (D_2), in line with previous results, show superior stability than D_1 or D_3 .

At further heat treatment Table XI shows that D and S assume significance and of the various silicones S_3 is the least stable; hence contributing significantly to yellowness.

Again Table XII shows that with longer heat treatment and at more elevated temperatures D and S are no more independent variables, but show interactions which make DS interactions of significance.

The fact that M did not show any significant yellowness contributions neither independently nor by interactions with other components, would seem to indicate that benzoic acid is the most stable component of the alkyd constituents, or its oxidative decomposition

products do not contribute, to any significant extent, a share in the yellowness developed in the enamel film.

The overall picture as depicted by the results of this experiment seem to indicate that :

(1) The monobasic acid whether used in one or the other of the three levels of concentration studied, made hardly any difference on the various properties of the copolymers.

(2) At elevated heat exposures, of the isomeric dibasic acids used, isophthalic acid produced enamels of superior properties to those of the other two isomers.

(3) Of the three silicones, there is no doubt that sylkyd 50 was inferior in its heat stability to S_1 and S_2 . On the other hand S_1 and S_2 produced no significant differences in copolymer properties neither during the early stages of heat exposure nor at higher temperatures.

These conclusions and results seem to be in full agreement with results that were obtained by a different approach in an earlier study (20).

TABLE X.

Analysis of variance : Yellowness at 225°C after 25 hrs.
of exposure.

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	17.852	8.926	---	4.46
D	2	117.528	58.764	---	4.46
S	2	31.303	15.652	---	4.46
MD	4	18.307	4.577	.270	3.84
MS	4	16.608	4.152	.245	3.84
DS	4	36.632	9.158	.540	3.84
MDS	8	135.689	16.961		
Total	26	373.920	118.189		

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	17.852	8.926	---	3.49
D	2	117.528	58.764	5.67 *	3.49
S	2	31.303	15.652	---	3.49
Error	20	207.236	10.362		

TABLE XI.

Analysis of variance : Yellowness at 225°C after 50 hrs.
of exposure.

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	8.02	4.01	---	4.46
D	2	167.76	83.88	---	4.46
S	2	107.21	53.60	---	4.46
MD	4	8.81	2.20	.17	3.84
MS	4	3.39	.85	.065	3.84
DS	4	139.92	34.98	2.66	3.84
MDS	8	105.15	13.14		
Total	26	540.26			

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	8.02	4.01	.31	3.49
D	2	167.76	83.88	6.52 *	3.49
S	2	107.21	53.60	4.17 *	3.49
Error	20	257.27	12.86		
Total	26				

TABLE XII.

Analysis of variance : Yellowness at 250°C after 25 hrs.
of exposure.

S.V.	D.F.	S.S.	M.S.	F.	F 5%
M	2	51.51	25.76	---	---
D	2	378.61	189.30	3.7	6.94
S	2	84.68	42.34	---	---
MD	4	56.61	16.15	---	---
MS	4	68.47	17.12	---	---
DS	4	204.17	51.04	4.96 *	3.84
MDS	8	82.39	10.30		
Total	26	926.44			

Effect of Various Polyols on Silicone-Alkyd Copolymers.

So far in this work TME., was the only polyol employed. From a previous study (20), it was ascertained that substituting glycols of various chain lengths for TME., did not increase materially thermal stability or flexibility of the copolymers. Resins using neopentyl glycol were found to be the best of the glycols studied up to a service temperature of 230°C. Since the polyhydric alcohol is considered the connecting link between the alkyd constituent and the silicone it was deemed worthy of exploring further its effect on the properties of the copolymers.

Comparative study using polyols of various chain lengths and functionality included 1, 2, 6 - hexanetriol, trimethylol ethane, trimethylol propane, pentaerythritol alone or mixed in definite proportions with neopentyl glycol and 1,5-pentane-diol. The respective formulations are shown in Table XIII. The results are given in Table XIV.

TABLE XIII.

Experimental Formulations for Studying the Effect of Polyols
On Properties Of Silicone - Alkyd Copolymers.

Exp. 104	Equivts.	Grams.	Exp. 105	Equivts.	Grams
Benzoic Acid	1.25	152.5	B.A.	1.25	152.5
Isophthalic Acid	2.00	166	Isophthalic Acid	2.00	166
1,2,6 Hexane triol	6.00	268	Neopentyl Glycol	2.00	103.0
Silicone : S ₁	2.75	495	Trimethylol Ethane	4.00	159.5
			Silicone : S ₁	2.73	492.0
Exp. 107	Equivts.	Grams	Exp. 108	Equivts.	Grams
Benzoic Acid	1.25	152.5	Benzoic Acid	1.25	152.5
Isophthalic Acid	2.00	166	Isophthalic Acid	2.00	166
Trimethylol Ethane	3.98	159.1	Penta erythritol	3.94	134
1.5 Pentane	1.99	103.6	Neopentyl Glycol	1.96	102.1
Silicone : S ₁	2.73	492.0	Silicone : S ₁	2.65	476.7
Exp. 100	Equivts.	Grams	Exp. 17	Equivts.	Grams.
Benzoic Acid	1.25	152.5	Benzoic Acid	1.25	152.5
Isophthalic Acid	2.0	66	Isophthalic Acid	2	166
Trimethylol Propane	6.01	268	TME	5.93	237.2
* Silicone : S ₁	2.76	497	S ₁	2.68	482

S₁ = phenyl ethoxy poly-siloxane (25% ethoxy).

TABLE XIV

No	Polyol	% So- lids.	A.N.	Gloss									Yellowness									
				Ethanol cc. equivlt.	Ini- tial	24hrs 225°C	48hrs 225°C	96hrs 225°C	24hrs 250°C	48hrs 250°C	72hrs 250°C	24hrs 275°C	48hrs 275°C	Ini- tial	24hrs 225°C	48hrs 225°C	96hrs 225°C	24hrs 250°C	48hrs 250°C	72hrs 250°C	24hrs 275°C	48hrs 275°C
17	TME	62.1	3.4	44	98	88	88	@	78	79	@	74	@	0	0	0	@	.049	.049	@	.088	@
100	TMP	68.0	9.5	32	100	94	92	90	75	--	--	--	--	0	.017	.035	.065	.228	--	--	--	--
104	Hexane Triol	62.0	10	22	97	68	63	@@	--	--	--	--	--	.046	.304	.300	--	--	--	--	--	--
105	TME NG	63.2	5.9	36	97	77	75	73	68	--	--	--	--	0	.059	.098	.111	.111	--	--	--	--
107	TME PD	57.8	9.4	40	94	68	67	64	64	--	--	--	--	0	.128	.127	.176	--	--	--	--	--
108	NG Pen- taeryth	63.0	6.5	29	97	90	88	84	84	82	80	71	64	0	0	0	0	.071	.112	.112	.114	.116

Hardness at 225°C

	Ini- tial	24hrs	48hrs	96hrs.
17	37	@	@	@
100	36	33	31	33
104	45	36	33	--
105	40	35	34	39
107	35	26	33	43
108	37	28	24	50

@ Values are not available

@@ Extensive peeling and cracking

-- Peeling and cracking complete.

Discussion Of Results.

In Copolymerizing alkyd and silicone resins the amount of alcohol liberated is normally taken as a measure of the extent of the alcoholysis reaction. Table XIV shows that for comparable formulations of the three triols investigated the amount of alcohol liberated was considerably more with TME than with trimethylol propane and was least with 1, 2, 6 - hexane-triol. This seems to be contrary to our expected stipulations that using longer chain triols may have less steric effects on copolymerization and therefore, may result in a greater extent of copolymerization and possibly a greater flexibility of the copolymers. This unexpected result may mean that steric effects are not significant in short chain triols and the extent of copolymerization is primarily determined by the average functionality of the reactants. It may also mean that the greater reactivity of the primary hydroxyl groups in TME and trimethylol propane is responsible for advancing the copolymerization reaction to imminent gelation before the less reactive secondary hydroxyl groups in 1, 2, 6-hexane-triol had chance to react.

All cured enamels in this study showed a high initial gloss. Fig., III shows the relationship between gloss and heating time at 225°C.

During a heating period of 96 hours, enamels containing trimethylol propane and TME retained high degree of gloss. On the other hand enamels containing 1, 2, 6 - hexanetriol showed a greater degree of decomposition as evidenced by an appreciably greater drop in the gloss curve and a significant increase on yellowness. Enamels containing mixed polyols showed intermediate gloss retention during the same heating period. It is worth noting that mixed formulations of TME and neopentyl glycol showed superior stability to those of TME and 1,5 - pentane-diol. This seems to be in agreement with previous (20) observations that stability varies in an inverse order with the glycol chain - length.

During heat exposures at 250°C there was a significant decrease in gloss for enamels containing TME and trimethylol propane; however, enamels that contained trimethylol propane started to show film failure, which precluded any gloss measurements after 24 hours of heat exposure. The only enamels which were able to stand a temperature of 275°C were those that contained TME and pentaerythritol with neopentyl glycol. This means that further investigation with mixtures of pentaerythritol and neopentyl glycol may reveal compositions of superior thermal stability added to a good film integrity.

Fig. 3. 39 a.
Gloss And Gloss Retention Of Various Polyols at 225°C.

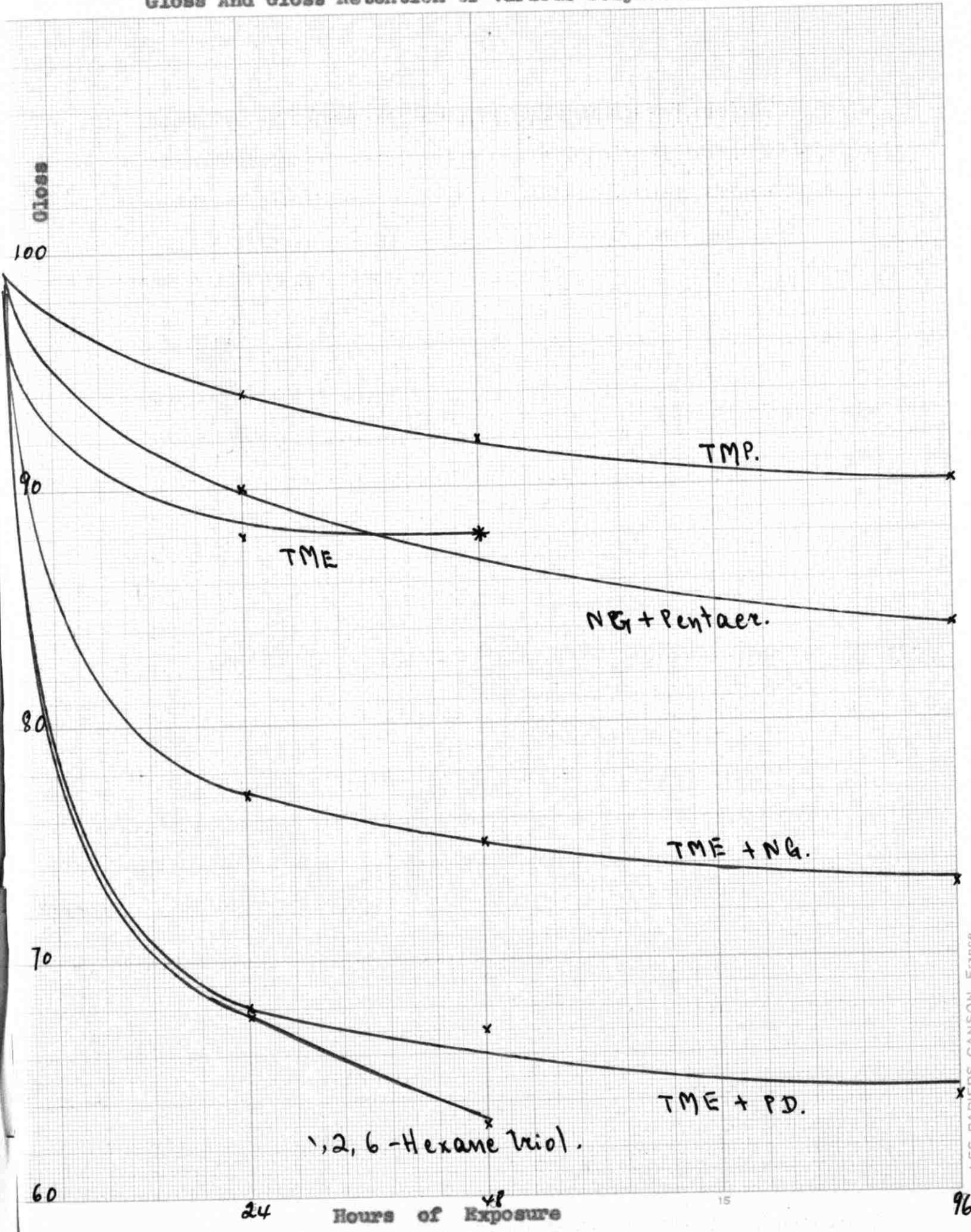


Fig. 4. 39 b.
Yellowness And Yellowness Retention Of Various Polyols at 225°C.

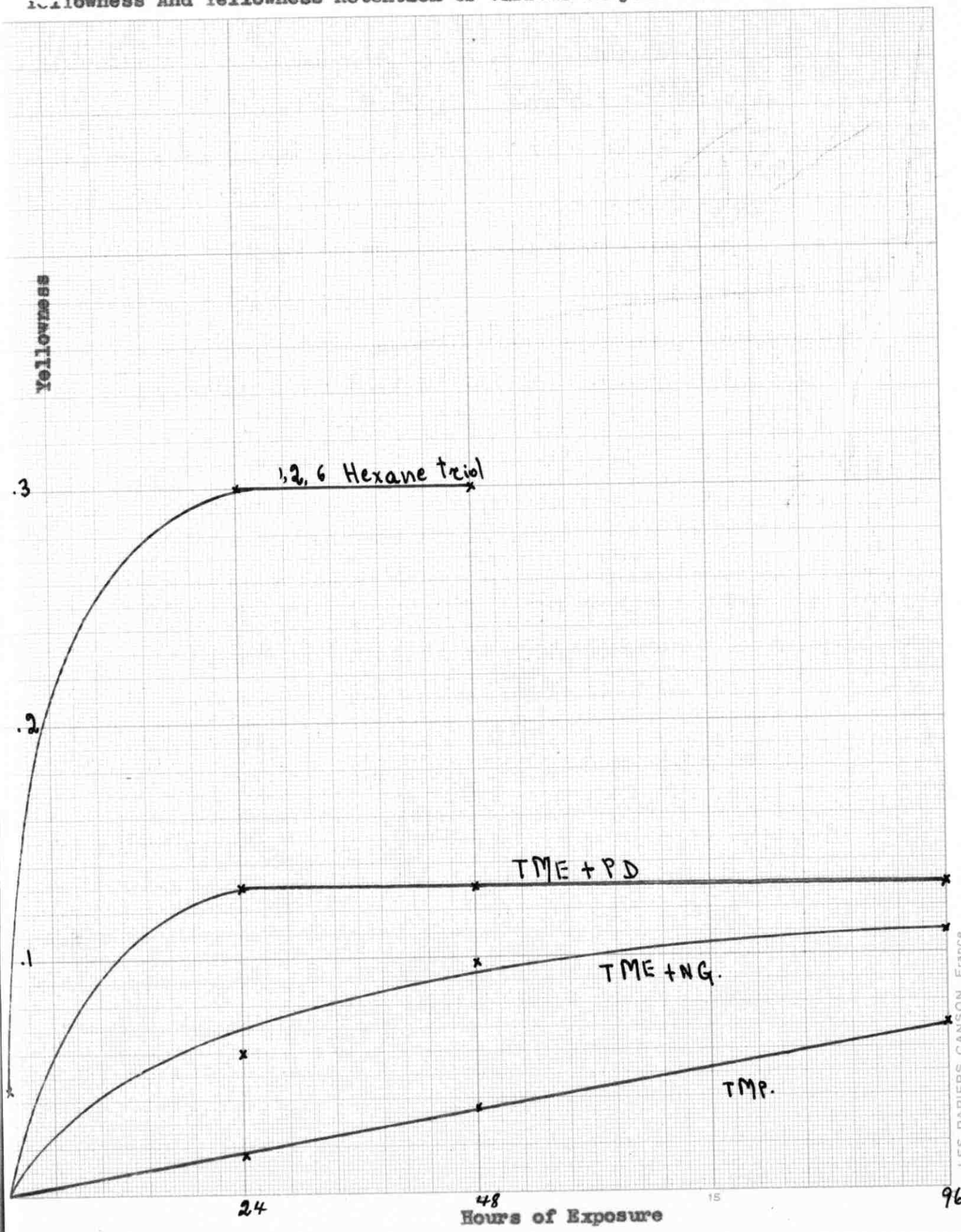


Figure IV shows the relationship of yellowness with heat exposure at 225°C. It gives evidence that supports conclusions made on gloss and gloss retention. For example, enamels containing 1, 2, 6 - hexane-triol which shows very poor gloss retention, exhibit a considerable increase on yellowness with heating time. This again seems to substantiate the fact that a decrease in gloss and an increase in yellowness are correlated with polymer degradation.

Although investigators differ in what fundamental property or properties are measured by hardness tests they seem to agree that hardness readings have served to trace and determine the rate of cure of surface finishes.

Table XIV shows that enamels of various compositions did not show any significant difference in hardness after curing. However upon heat exposure hardness tests showed a decrease in hardness to a minimum, followed by an increase in hardness. No correlations were obtained as to the rate of reaching the minimum nor the rate of increase thereafter. However, the decline in hardness is most probably due to degradation reactions that involve, primarily, the alkyd constituents and permit a rearrangement of the residual chains which show lower hardness than the highly cross linked copolymers. Consequently the

two reactions taking place on the panel namely copolymerization and degradation proceed simultaneously, but at different rates causing the enamel film to pass thru a minimum hardness.

Comparative Study Of the Effect of Monobasic acids on TME
and Trimethylol Profane.

In a previous study (20) using TME as the polyol, it was found that the heat life of silicone-alkyd resins increased exponentially with the decrease in the monobasic acid chain length. However, with monobasic acids such as butyric and caproic, this improved stability of the resins was counteracted by a decrease on the flexibility of the resin which resulted in brittleness and finally cracking of the enamel film from the substrate.

A series of experiments were designed to find out whether analogous correlations of the effect of monobasic acid constituent on silicone alkyd properties exist in a system using trimethylol propane instead of TME. The monobasic acids used for the comparative study were benzoic acid, p-tertiary butyl benzoic acid, caproic acid and trichloroacetic acid.

Acetic and formic acids were not formerly used as alkyd constituents due to their high volatility at the alkyd processing temperatures of 180-250°C. Trichloroacetic acid which boils at 196-197°C can be processed with the alkyd constituents without serious losses during the reaction period. Besides, the acid is a strong acid and by its use the effect of the strength of the monobasic acid on the rate of esterification as well as the properties of the alkyd resins produced will be ascertained. The formulations used

are found in Table ~~XV~~. The results are given in Table XVI.

TABLE XV.

Exp. 100	Equivts.	Grams	Exp. 102	Equivts.	Grams
Benzoic Acid	1.25	152.5	Caproic Acid	1.25	145.3
Isophthalic Acid	2.0	166	Isophthalic Acid	2	166
Trimethylol propane	6.01	268	Trimethylol propane	5.95	266
Silicone : S ₁	2.76	497	Silicone : S ₁	2.70	486.8
Exp. 101	Equivts.	Grams	Exp. 103	Equivts.	Grams
Trichloro Acetic Acid.	1.25	204.3	P - tertiary-butyl benzoic acid.	1.25	222.5
Isophthalic Acid	2.0	166	Isophthalic Acid	2.0	166
Trimethylol propane	6.36	284	Trimethylol propane	6.47	289
Silicone : S ₁	3.11	559	Silicone : S ₁	3.22	581

S₁ phenylethoxy polysiloxane (25% ethoxy).

Discussion of Results

The results shown in Table XVI., seem to be comparable with those obtained in a system using TME. All enamels had a high initial gloss. Enamels containing caproic acid proved to be thermally less stable than those that contained p - tertiary butyl benzoic acid and benzoic acid. This was clearly demonstrated by a steep decrease in gloss with time at a temperature of 225°C. This decomposition was manifested by a shorter heat life and a higher degree of yellowness.

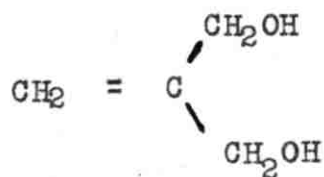
Of the two aromatic monobasic acids, again, enamels containing benzoic acid were superior in gloss, color retention and heat life.

In processing alkyds containing trichloro-acetic acid excessive decomposition changed the reacting constituents, within half an hour of initial heating, to a highly viscous brownish-black polymer mass, and a yellowish distillate. Such unusual decomposition in the preparation of the alkyd precluded any further work with it.

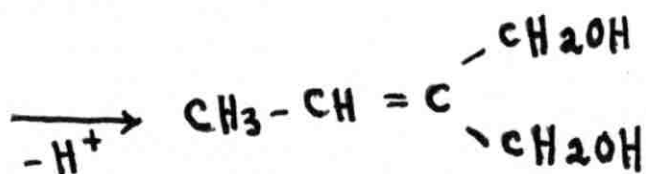
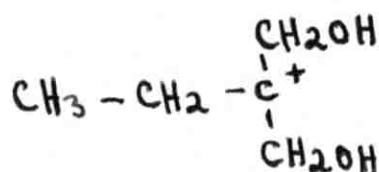
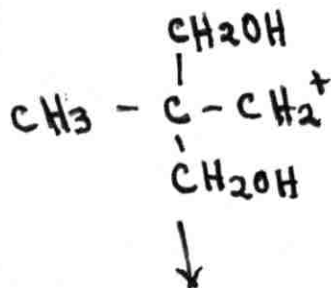
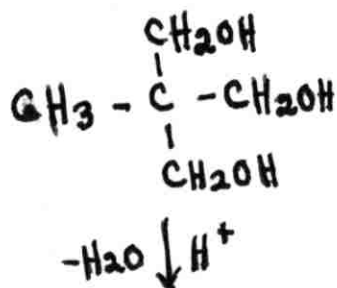
To find out whether the acid strength, the monobasic acid was responsible for the serious decomposition in the alkyd processing, comparable experiments were run using trichloro-acetic acid and TME, dichloroacetic acid and TME, p-nitrobenzoic acid and TME, p-nitrobenzoic acid and pentaerythritol, and finally dichloro-acetic acid and penta-erythritol. Invariably, in all these alkyd polymerizations we obtained a brownish-black polymer mass

and a yellowish distillate.

To investigate the nature or mechanism of this polymer decomposition was outside the scope of this research. However, upon running few tests on the yellow distillate it was found that it decolorizes readily KMnO_4 , but does not add free bromine. It is known that organic compounds containing the following configuration:



reduce KMnO_4 but do not add free bromine. Hence, a possible interpretation of the decomposition that was demonstrated by the action of strong monobasic acids on the various polyols may be as follows :



Partly decomposes,
partly polymerizes by
addition, and partly
by condensation.



TABLE XVI.

No.	Monobasic Acid	A.N.	Alcohol cc./equivlt.	Gloss					Yellowness						
				Ini-tial	24hrs 225°C	48hrs 225°C	96hrs 225°C	24hrs 250°C	48hrs 250°C	Ini-tial	24hrs 225°C	48hrs 225°C	96hrs 225°C	24hrs 250°C	48hrs 250°C.
100	Benzoic Acid	9.5	32	100	94	92	90	70	---	0	.017	.017	.65	.230	---
103	p-t-butyl benzoic	6.0	32	99	82	78	76	68	61 @	0	.103	.103	.173	.203	.254
102	Caproic	10	29	92	78	75	57 @	--	--	0	.203	---	---	---	---
101	Trichloro-acetic.@@	--	--	--	--	--	--	--	--	--	---	---	---	---	---

Hardness at 225°C

	Initial	24hrs	48hrs	96hrs	
100	36	33	31	33	
103	30	32	36	--	@ Cracking and peeling extensive.
102	37	28	25	--	-- Cracking and peeling complete.
101	--	--	--	--	@@ After half an hour of processing, excessive decomposition precluded the use of the alkyd.

Raw Materials.

Benzoic Acid : C.P., Merch.

Isophthalic acid : Technical, Oronite chemical company.

Phthalic anhydride : Technical, Monsanto Chemicals and Plastics.

Terephthalic acid : Technical, Du-Pont De Nemours & Co.

(The acid was of yellowish color. It was purified by acetone extraction in a soxlet apparatus.)

Caproic acid : C.P., Eastman Kodak.

p-tertuary-butyl benzoic acid : Technical., Shell Chemical corporation.

p-nitrobenzoic acid : C.P. Merck.

Dichloro acetic acid : C.P. Fisher Scientific Company.

Neopentyl glycol : C. P. Eastman Kodak.

1, 5-pentane-diol : Technical, Carbide and Carbon Chemicals.

TME : Technical, Hyden Chemical Corporation.

Trimethylol propane : Technical, Celanese Chemicals.

1, 2, 6 - hexane-triol : Technical, Carbide and Carbon Chemicals.

Pentaerythritol : C. P., Eastman Kodak.

Titanium dioxide : Technical., Du-pont De Demours and Company.

Phenyl-ethoxy-polysiloxane (25% ethoxy). Union Carbide and Carbon Corporation.

Phenyl (60) dimethyl (20) diphenyl (20) ethoxy polysiloxane (20% ethoxy) Union Carbide and Carbon Corporation.

Trimethoxy-triphenyl-dimethyl-trisiloxane (20% methoxy) (Sylkyd 50) technical grade. Dow Corning Co.

Diisobutyl Ketone : Technical., Eastman Kodak.

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