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Marshall Research and Development Laboratory Report

SOLVENT FREE LIQUID COATINGS

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ABSTRACT

A lead to solvent free coatings has been found. It consists of a two package systems and involves two reactions: a very fast reaction of an epoxyide with an acid to build viscosity, and then a conventional polymerization or air cure to cross-link the film. Other approaches are discussed.

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8/25/71

SOLVENT FREE LIQUID COATINGS

INTRODUCTION

The drive for clean air has resulted in the promulgation of nationwide air quality standards that, in many areas, are close to the natural background. As a result, we can expect that legislation to meet these standards may force some manufacturers to use finishes systems containing no or very little solvent. As an arbitrary bench mark, any composition containing 15% by weight or less volatile solvent will be included in the low solvent containing category.

Of the various routes to low solvent systems the solvent free liquid route has been getting the least attention at this time, although several years ago it was the subject of a large research effort. One of the major problems encountered at that time was the difficulty of spraying low viscosity liquids that had no opportunity for a rapid viscosity increase, once they were applied to the work. The addition of high molecular weight polymers or thixotropic agents was of some help, but generally at the expense of some other important property, such as gloss.

A need exists for a better approach to solvent free, liquid (100% "solid" liquids) systems, that will allow them to be sprayed without undesirable additives.

OBJECTIVE

The objective of this work is the development of leads to solvent free, liquid coatings that can be sprayed without the addition of high molecular weight polymers or thixotropic agents.

SUMMARY AND CONCLUSIONS

A combination of liquid, reactive materials, based on ester acids of maleic anhydride and a cycloaliphatic epoxy resin, Carbide's ERL 4221, was found to be sprayable and to increase in viscosity at a rate sufficiently high to prevent sagging. With proper catalysts low bake coatings (90 minutes x 150°F or 30' x 200°F) were developed. Room temperature "air dry" was achieved in an inert atmosphere and approached but not reached in the normal atmosphere.

Application depends on the blending of two streams either in or out of a spray gun. A two orifice gun seems to be the best at this time. Ingredient costs are feasible; our most promising composition is $0.60/lb., and process steps are simple.

Little or no information on chemical resistance, durability, or pigmentation has been obtained so far.

ACTION TAKEN OR PROPOSED

We will continue to explore this lead. Our program is to define the ranges of suitable raw materials, and to develop information needed for defining potential applications.

PATENT SITUATION

No patent proposals have been written so far, but we will plan to make such proposals as soon as the scope of this discovery has been defined. Our strategy will be to claim the invention in its most fundamental terms, such as acid-epoxide, functionality, and cross-linking reactions. We believe that several cases may have to be developed.

PUBLICATION STATUS

No publication of this work is currently contemplated.

ACKNOWLEDGMENTS

I wish to acknowledge the diligent and imaginative assistance of Harry Mc Henry, who contributed to the experimental work with enthusiasm and imagination.

DISCUSSION

Of the various possible methods of providing decorative or protective coatings, solvent free liquids have advantages in several end uses. Powder coating or water borne dispersions of industrial quality require heating to high temperature for coalescence and film formation. This is impossible in certain industries, such as furniture, maintenance, transportation and refinish. Even for industries that can use heat for curing finishes, liquids would still offersuch features as minimal new investment, familiar techniques, and use of existing facilities.

The majority of all industrially used coatings are applied by the spraying of solvent based finishes. The solvent in a correctly formulated system reduces the viscosity of the finish so that it atomizes properly, but evaporates fast enough so that the applied paint is sufficiently viscous not to run off the work. In solvent free liquid coatings this mechanism of rapidly increasing the viscosity after exit from the gun is not available. Since a low viscosity is needed for good atomization, problems are encountered when such coatings are sprayed.

There are many techniques that can be used to increase the viscosity of a liquid. These can be either physical or chemical. Among the physical methods are evaporation of a volatile solvent, addition of high molecular weight polymer, addition of a thixotropic agent, change from dispersion to solution of polymers and change from sol to gel. Chemical methods of increasing viscosity include an increase in molecular weight, a change in solubility by increasing or decreasing the number of functional groups, or by changing the nature of functional groups by chemical reactions. Examples are salt formation or hydrolysis of salts, reaction of isocyanate with an amine or hydroxyl group, loss of CO_2 from an acid, etc.

Increase in molecular weight of a low molecular weight liquid can be achieved by polymerization, either by adding an initiator or by mixing two reactive components. If the polymer is formed very rapidly or if it crosslinks early in the polymerization, the final appearance may be poor since insufficient time will be available for the film to flow out and level. If the reaction is slow the fluid will sag or run. A very narrow balance appears to be needed.

This was recognized by Ikeda[1] when he was scouting for new air drying finishes which dry by vinyl polymerization. He suggested that two distinct reactions be used; one, which would cause an increase in viscosity, and a second which would then give a dry, hard, crosslinked film. The initial reaction could be fast, but the increase in viscosity would be limited because no high molecular weight polymer could form. This would allow the film to flow and level but not sag. The second reaction would be a slower one, and it should lead to the final film properties.

This concept was felt to be the most likely route to low solvent liquid coatings, and possibly to solvent free systems. The requirements for the materials to be used have to include:

1. Viscosity low enough to spray
2. Rapid viscosity increase after spray
3. Final film with acceptable properties
4. Low toxicity
5. Reasonable economics

Although a one package system would be the most desirable, a two package system seemed easier to achieve, and it was decided to try to develop some leads for this approach.

A number of reactions were considered for both the viscosity increase (Step 1) and the final cure (Step 2). In order for the latter to have the broadest range of use an oxidative or polymerization reaction was deemed desirable. Acrylic systems generally polymerize readily, but are inhibited by oxygen, especially at low temperatures. References in the literature[2] suggest that the inclusion of ethers, especially allyl ethers, which need O_2 to dry, can be used to overcome or minimize this inhibition. We therefore tried to develop systems that could dry oxidatively or by vinyl polymerization for the film forming reaction. Not many allyl ethers containing other functional groups are commercially available, but we obtained the following: allyl glycidyl ether, glyceryl allyl ether[1,2] diallyloxy ethane, and trimethylol propane diallyl ether monomethacrylate. The first two can be incorporated into oligomers or low molecular weight polymers and the latter two can perhaps be used as reactive diluents or viscosity reducers.

Oligomers containing 2 or more reactive unsaturated groups can generally be cured in air at a reasonable temperature, so that the final curing step does not seem a pressing problem during the initial scouting work. The major emphasis must be placed on the search for a technique of rapidly increasing the initial viscosity from the spray viscosity to some higher viscosity which will be sufficient to prevent sagging.

The following reactions were considered:

1. $ROH + Ti(OR_4') \longrightarrow (RO)_n\ Ti(OR')_{4-n} + n\ R'OH$

2. $ROH + Si(OEt)_4 \longrightarrow (RO)_n\ Si(OEt)_{4-n} + n\ EtOH$

3. RCO_2H + Metal salt $\rightarrow$ (RCO_2^-) Me

4. $RCO_2H + C\overset{O}{\diagup\diagdown}C \longrightarrow R\overset{O}{\overset{\|}{C}} - O\text{-}C\text{-}C\ OH$

5. $ROH + Y(NCO)_n = (RO\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N})_n Y$

The major requirement for these and similar reactions is that the reaction is fast and stoichiometric, that is, not a polymer forming process, so that the increase in molecular weight (or viscosity) of the initial reaction can be controlled.

A number of attempts were made to prepare derivatives of hydroxy-ethyl acrylate, trimellitic anhydride or phthalic anhydride and allyl glycidyl ether. It was hoped that by combining allyl ether and acrylate in the same molecule a room temperature air curing system could be developed. The free acid or hydroxyl groups could then be used to react with a multifunctional molecule to get a rapid increase in molecular weight and viscosity.

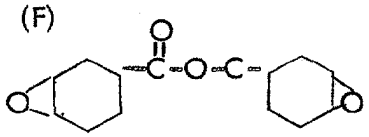
Unfortunately, all systems were either high so in viscosity as to require dilution with solvent to be sprayable or pourable, or they gelled quickly. (A Table I)

Some of the materials air dried at room temperature with Co drier. The same general structure (B), but with glycidyl methacrylate (B) replacing allyl glycidyl ether (A), did not air dry. (Table 1) This seemed to confirm our expectation that a combination of allyl ether with an acrylate ester would overcome air inhibition. Unfortunately, the diallyl ether monomethacrylate of trimethylol propane (commercial preparation containing an inhibitor) did not air cure. Attempts to remove inhibitor by treatment with activated charcoal did not increase the drying powers. Other factors, such as viscosity, which was very low for the TMP derivative, may also play a part.

Attempts to prepare low molecular weight polyesters with acrylate functions failed because of high viscosity, which may have been due to partial polymerization of the acrylate. (D, E)

While ethyl acrylate or methyl acrylate undergo facile ester interchange with many alcohols we were not able to affect this reaction with glyceryl allyl ether. (C) Several catalysts, including sodium metal, sodium methylate, methane sulfonic acid, dibutyl tin oxide, toluene sulfonic acid and titanates were tried without notable success. The reason for the difficulty is not understood.

The most promising results were obtained from the reaction of hydroxethyl acrylate and maleic anhydride. This adduct forms rapidly and quantitatively at 100-110°C in the presence of a small quantity of sodium acetate. The resulting low molecular weight acid is fluid and very reactive with cycloaliphatic epoxides such as Carbide's ERL 4221. (F)



When mixed in a 2/1 molar ratio the viscosity of the mixture increases rapidly. Even in 15 g quantities the reaction is exothermic. The increase in viscosity with time was determined in a Gardner-Holt tube, as shown in Figure 1.

Limitations of the ERL 4221 Systems

Cycloaliphatic epoxides are considerably more reactive toward carboxylic acids than straight chain, terminal epoxides. Nevertheless, at room temperature, without catalysts, the reaction is slower than desired. Several acids were tested, and it appears that reactivity is a function of acid strength and concentration. While acryloxethyl mono maleate, when blended with ERL 4221, causes an exotherm and leads to a rapid increase in viscosity (from 3 stokes to 16 stokes in 15 minutes) acryloxethyl monosuccinate which is almost identical in molecular weight and structure does not seem to react at all in 15 minutes. One obvious difference is acid strength. The ionization constant K_A for the first acid group of maleic acid is 142×10^{4} while for succinic acid K_A it is 0.7×10^{-4} or smaller by a factor of $\frac{1}{200}$. Similarly, tall oil fatty acid (K_A 0.2×10^{-4}) did not react appreciably in one week. In this case both concentration and acid strength are lower, since the equivalent weight for the maleate is 214 and for the fatty acid about 280. A composition containing 2.5 moles TOFA, 1 mole PE, cooked to $A^{\#}$ -4 and reacted with 1.4 moles maleic anhydride had an acid number of 93. This reacted with ERL 4221 but much slower than the higher acid number adduct from HEA, probably because of the lower carboxyl concentration.

It would be desirable if the initial viscosity rise could be accelerated, even for the EHA/MaAnadduct. Several routes are possible and have been explored. The addition of a catalyst for the acid-epoxide reaction is one approach. We examined chromium diisopropyl salicitate (CrDIPS), H_2SO_4 and CH_3SO_3H. Of these H_2SO_4 was the most effective (Figure II). After 2 minutes (first measurement) the viscosity was nearly twice that without the acid and it continued to rise rapidly. Methane sulfonic acid CH_3SO_5H was less effective, but did give some improvement after 6-8 minutes. CrDIPS showed no effect either viscosity or the decrease in acid number (Figure III). The two curves are about as reproducible as the method of measurement permits.

Another possible method of hastening the rate of viscosity increase is to add a small quantity of a difunctional molecule. We prepared diethylene glycol bis (acid maleate) and added 10 mole % of this to HEA/MaAn. We observed to a definite effect, which was most noticeable after about 6 minutes, but we did not get the real fast initial increase we hoped for. (Figure I) Other catalysts will have to be tested.

Cure and Film Properties

Most of the work on developing the optimum film properties so far has been carried out with the HEA/MaAn adduct. Mixtures of this adduct with ERL 4221 when baked at 300°F for 30 minutes with Co dryer gave tough, hard, adherent films on glass, aluminum or bonderite steel. They are slightly brittle but not unusually so for unsaturated systems. The surface is readily marred, probably due to oxygen inhibition of the polymerization at the surface: Other driers tried were Mn, Pb, Ca. Of all these Mn seemed to give the best surface cure. (Table II) At 200°F or lower no polymerization occurred and the films remained liquid.

If free radical initiators were used at 200°F no appreciable cure was observed with Vazo®, di-t-butyl peroxide or cumene hydroperoxide. Addition of 1% MEK peroxide gave a slightly tacky film. The combination of various peroxides and Mn drier gave tacky only films in the case of MEK peroxide or cumene hydroperoxide. MEK peroxide and Co naphthenate gave tack free films at 200°F with one batch of HEA/MaAn adduct, but with another batch the films retained a slight surface tack, which disappeared after a few days.

If we want to consider these materials for furniture finishes bakes below 150°F become mandatory. The Co naphthenate/MEK peroxide curing system was found to cure at 90 minutes at 150°F to a tack free finish which had excellent adhesion to maple, and could be sanded and rubbed after 4 hrs. A repeat with a new batch of adduct gave a slightly tacky film. Apparently the two batches of adduct were not identical.

The mixed systems adduct-cobalt drier/Epoxide-peroxide has a pot life of 15 minutes or less at room temperature. When a film is dried in air at room temperatures it does not become tack free for weeks; when the film is kept in an oxygen free atmosphere it dries tack free in less than one hour. Oxygen inhibition appears to be very pronounced.

In an effort to improve the low temperature drying of these systems and to overcome oxygen inhibition a composition based on drying oil fatty acids was prepared. The reaction of 1 mole pentaerythritol (PE) with 2.5 moles tall oil fatty acids (TOFA) gave an ester with an average of 1.5 hydroxyls/molecule. This was reacted with 1.4

moles MaAn. This composition had a very high viscosity (15 stokes) and an acid number of 93. When mixed with ERL 4221 the viscosity increased, although more slowly than with the HEA adduct. This composition set up at room temperature but did not become tack-free in 2 days. At a 200°F bake it became almost tack free and gave a slightly yellow, soft film.

We tested blends of the TOFA and HEA adducts. They have limited compatibility, so except for small quantities of one in the other cloudy films result. These do not air dry to tack free films, and although there is some cure at 200°F, most of the films are tacky. The HEA adduct by itself at 200°F show practically no cure with Co dryer. Only the compositions containing 10 and 5 mole % of TOFA adduct were tack free after this low bake (Table IV). A more rapidly drying composition seems possible through this approach, but the films are too cloudy for many uses.

The addition of MEK peroxide to low TOFA adduct containing compositions gave very rapidly gelling mixtures. These dried to tack free film at 200°F. (Table IV) on overnight air dry.

Costs

Ingredient costs have been estimated for several compositions. As applied (complete mixture) the HEA/MaAn adduct reacted with ERL 4221 costs about 60¢/lb. Very little processing is necessary, since the reaction of HEA with MaAn takes 30 minutes at 100°C. The TOFA product has an ingredient cost of less than 30¢/lb. and only alkyd technology is used, so processing costs should be low.

Application

One major objective of this work was to develop leads for sprayable systems for our scouting work. We generally mixed liquid ingredients and made draw downs on panels. However, one attempt was made to spray the EHA/MaAn adduct with ERL 4221. We used two pressure pots and a 2 orifice gun. The composition was catalyzed with 0.1% Co in the acid portion and 1% MEK peroxide in the epoxide portion. Pot pressures were adjusted individually to give a ratio of about 4/3 adduct/epoxide. This necessitated a pressure of 7 lbs. for the epoxide and 50 lbs. for the adduct. Air pressure to the gun was 50 lbs. The gun was a special one built for Du Pont some time ago. The pressure differential is due to the differences in the size of the orifices.

The liquids broke up well in the fan and mixed sufficiently so that the systems cured on baking. One coat (1 series of passes with about 50% overlap) deposited one mil on the work. Application of 2 coats (1.9 mils) was possible with only very slight sagging observed. The major problem encountered was very poor wetting of all surfaces. The films showed severe crawling and fish eyeing. This may have been due to incomplete mixing or rapid viscosity build up or too high a surface tension. This has not

been observed on draw downs, so further work to find the causes will be needed.

Pigmentation

Only one attempt was made to prepare a pigmented product. A white base was prepared with TiO_2 in the adduct and this was mixed with the ERL 4221 and draw down made. The system was catalyzed with Co and MEK peroxide. The panels were glossy until baked, then a surface structure developed that caused reduced gloss. Longer flash times (up to 16 hrs.) reduced but did not eliminate this effect. No reason can be given at this time.

EXPERIMENTAL DETAILS

Preparation of acryloxyethyl monomaleate. NB9952, p.24

1066g of hydroxyethyl acrylate and 18.4g of sodium acetate were heated to 100°C in an inert atmosphere; 900g of powdered maleic anhydride were added over 10 minutes, the mantle having been turned off; after an additional 10 minutes heating was resumed and continued for 30 minutes. The reaction was finished. Acid number 262, viscosity 2.7 stokes.

Diethylene glycol bis (mono acid maleate). NB 9952-23.

A mixture of 106g diethylene glycol and 2g sodium acetate was heated to 105°C in an inert atmosphere with stirring. The mantle was lowered and 196g maleic anhydride (powdered) was added in 8 mins. The temperature dropped to 85°. Heating was resumed and the temperature was kept between 120 and 110° for 20 minutes. The product was cooled. AN-376.

Pentaerythritol Tall Oil fatty acid ester - Maleic anhydride adduct.

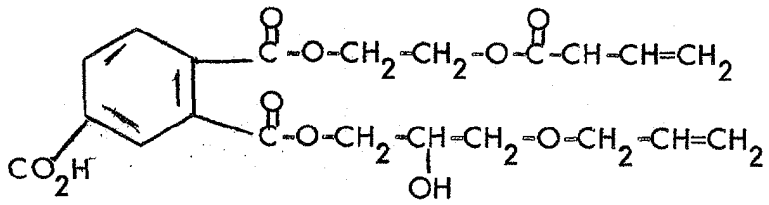
NB 9952 p. 25-26
350g H 663 TOFA (1.25 moles)
68g G419 PE (0.5 moles)

The mixture was heated to 230°C with stirring under an inert gas blanket and water removed. About 17g water was recovered after 1-1/2 hrs. above 190°C (Theory 22.5). After 2 hrs. the acid number was 8 and the reaction was cooled. Final acid number was 4, GH viscosity-G; (1.6 stokes). The product was slightly cloudy so it was filtered; 360g were recovered.

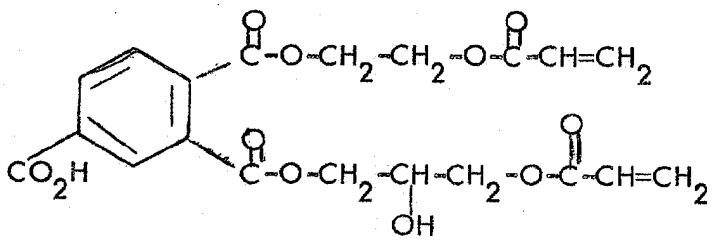
300g of filtered material was heated to 100° and 54.3g MaAn added over 7 minutes. After an additional 30 minutes at 100°. The acid# was 93 (theoretical) so the reaction was stopped. On cooling crystals precipitated that were identified as MaAn by titration. To complete the reaction 1g Na acetate was added and the heating at 100° resumed for an additional hour. On cooling again no further precipitate appeared and the reaction was considered complete. Acid number was still 93, viscosity 15 stokes.

TABLE I

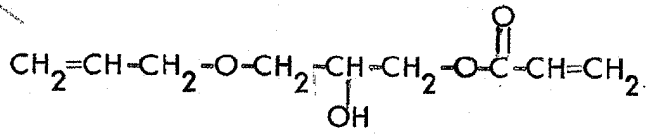
trimellitic anhydride
allyl glycidyl ether A
hydroxy ethyl acrylate



trimellitic anhydride
glycidyl acrylate B
hydroxy ethyl acrylate



glyceryl allyl ether
ethyl acrylate C



phthalic anhydride
glyceryl allyl ether D
hydroxy ethyl acrylate

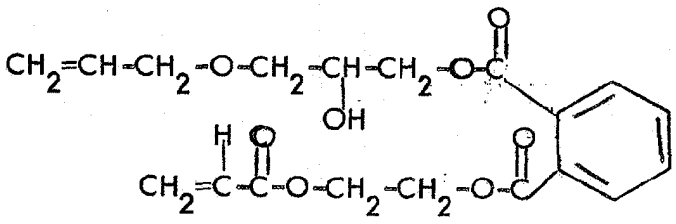
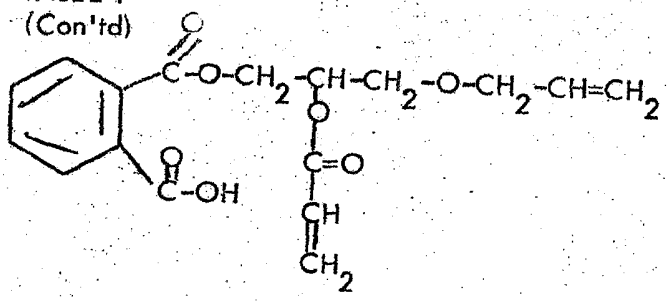


TABLE I
(Con'td)

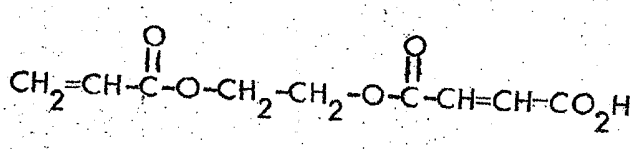
allyl glycidyl ether
acrylic acid
phthalic anhydride

E



hydroxy ethyl acrylate
maleic anhydride
ERL 4221

F



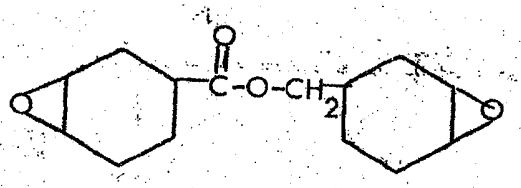


TABLE I - RESULTS

A) Benzyl trimethyl ammonium hydroxide used as catalyst. Product is viscous and produces a hard brittle, yellow film when baked 20 min. x 300°F. Also cures to hard slightly flexible film in five hours air drys with 1.0% cobalt drier. Product is unstable gels in 1 week.

B) Benzyl trimethyl ammonium hydroxide used as catalyst. Product is extremely biscous and produces a hard, tough, flexible film when baked 20 min. x 300°F. Would not air dry with cobalt napthenate.

C) Catalysts tried: Sodium metal, sodium methylate, methane sulfonic acid, toluene sulfonic acid, dibutyl tin oxide, TIPT. Methane sulfonic acid gave best conversion. Light greenish slightly viscous liquid that does not cure when baked 20 min. x 300°F.

D) Used toluene as carrier for H_2O. Used PTSA as catalyst. Batch has to be distilled. Final product is very viscous and cures to hard, tough finish when baked 30 min. x 325°F. Produces good tough film in 2 days air dry with 1.0% cobalt napthanate.

E) Catalysts tried: Benzyl trimethyl ammonium hydroxide, methane sulfonic acid, Cr DIPS. Allyl gylcidyl ether-acrylic acid reacted well. Pththalic anhydride would not react with the AGE/AA product. Unsuccessful.

F) HEA/Maleic anhydride reaction catalyzed with sodium acetate. Very fact reaction.. Final half - ester slightly viscous. Cures to hard tough finish when combined with ERL 4221 and baked x 200°F using catalysts. Air inhibited.

TABLE II

THE EFFECT OF VARIOUS NAPTHANATE DRIERS ON
FILM PROPERTIES OF ACID POLYMER/EPOXY SOLVENTLESS FINISH

Code	9655-204	ERL 4221	% Napthanates				Results (30 Min. x 300°F)
			Cobalt	Manganese	Calcium	Lead	
9952-12-1	4.0	3.0	0.1	-	-	-	Hard, slightly brittle film, slightly yellow, mars easily
-2	"	"	0.05	-	-	-	" " " " " " " "
-3	"	"	-	0.1	-	-	" " " " " " ,does not mar
-4	"	"	-	0.05	-	-	" " " " " " " " "
-5	"	"	-	-	0.1	-	Tough, slightly tacky, slightly yellow, mars easily
-6	"	"	-	-	0.05	-	" " " " " " "
-7	"	"	-	-	-	0.5	" " " " " " "
-8	"	"	-	-	-	0.1	" " " " " " "
-9	"	"	-	0.05	-	0.5	Tough, slightly brittle, mars easily, yellows

Note: None of the above formulations cured at room temperature or during a 30 min. x 175°F bake.

9655-204 - Hydroxyl ethyl acrylate/Maleic Anhydride = 116/98 AN-279

ERL-4221 - Union Carbide, Acid reactive cycloaliphatic epoxy resin

TABLE III

VARIOUS PEROXIDES AS CATALYSTS FOR ACID POLYMER/EPOXY SOLVENTLESS FINISH, WITH AND WITHOUT MANGANESE NAPTHANATE

Code	9952-10	ERL-4221	% Vazo®	% di-tert butyl Peroxide	% MEK Peroxide	% Cumene Hydroperoxide	% Manganese Napthanate	Results 30 x 200°F
9952-15-1	4.0	3.0	-	-	-	-	-	Did not form film
-2	"	"	1.0	-	-	-	-	" " " "
-3	"	"	-	1.0	-	-	-	" " " "
-4	"	"	-	-	1.0	-	-	Very slight tacky film
-5	"	"	-	-	-	1.0	-	Did not form film
-6	"	"	-	-	-	-	0.05	" " " "
-7	"	"	1.0	-	-	-	0.05	" " " "
-8	"	"	-	1.0	-	-	0.05	" " " "
-9	"	"	-	-	1.0	-	0.05	Formed tacky film
-10	"	"	-	-	-	1.0	0.05	Formed slightly tacky film

Note: None of the above formulations cured at room temperature

9952-10 = Hydroxy ethyl acrylate/Maleic Anhydride = 116/98 AN=263

ERL-4221 = Union Carbide, Acid reactive cycloaliphatic epoxy resin

TABLE IV

BLENDS OF 25-2/24[1] AND ERL 4221

#	Mols TOFA Adduct	Mols HEA Adduct	Weight/5 g ERL-4221 TOFA Adduct	Weight/5 g ERL-4221 HEA Adduct	Compatibility[2]	Visc.[3] with time (Min.) In.	5	10	25	Cure 200°F	Cure RT/24 Hrs.
1	1	0	22	0	Comp.	10	10.7	15.4	46.3	V. Sl. T.	Tacky
2	0.8	0.2	17.6	1.33	Sl. Inc.	8.0	10.7	12.9	27.0	Sl. T.	"
3	0.6	0.4	13.2	2.7	Inc.	6.3	9.8	10.7	27.0	"	"
4	0.4	0.6	8.8	4.0	Inc.	5.8	6.3	9.8	17.6	"	"
5	0.2	0.8	4.4	5.2	Inc.	6.3	6.3	11.7	55.0	"	"
7	0.1	0.9	2.2	6.0	Inc.	4.4	4.7	9.8	44	V. Sl. T.	V. Tacky
8	0.05	0.95	1.1	6.3	Inc.	3.4	3.6	6.3	46.3	Tack Free	"
6	0	1	0	6.7	Comp.	3.0	3.2	5.8	41.0	Liquid	Liquid
11	Same as 6 but with MEK peroxide									Tack Free	V. Tacky
12	Same as 7 but with MEK peroxide									"	Sl. Tacky
13	Same as 8 but with MEK peroxide									"	Sl. Tacky

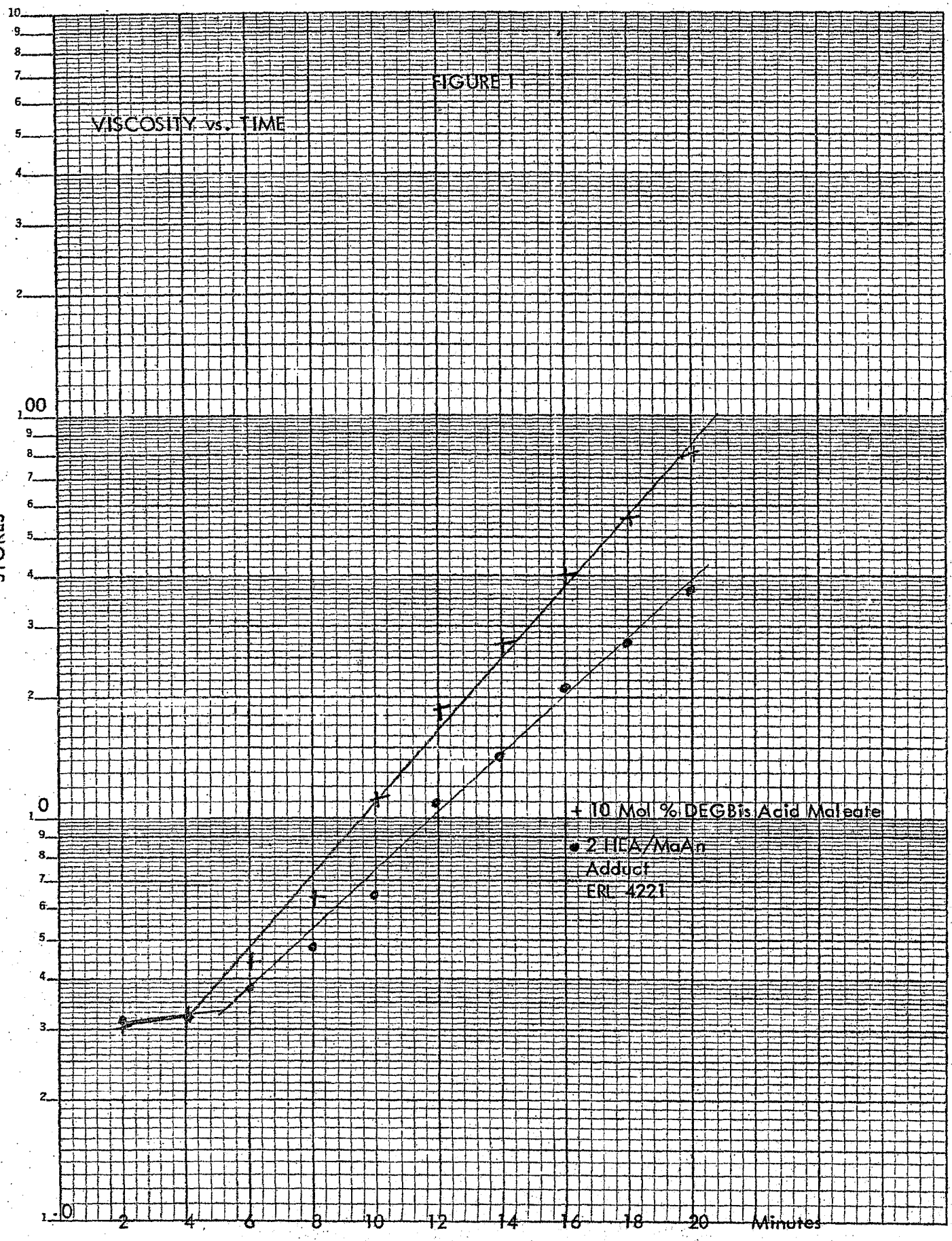
(1) 25-2 - Adduct of PE with 2.5 mols TOFA and 1.4 mols mal. anhyd.

24 " of 1 mole HEA with 1 mole mal. anhyd.

(2) of dry film

(3) in stokes

FIGURE 1



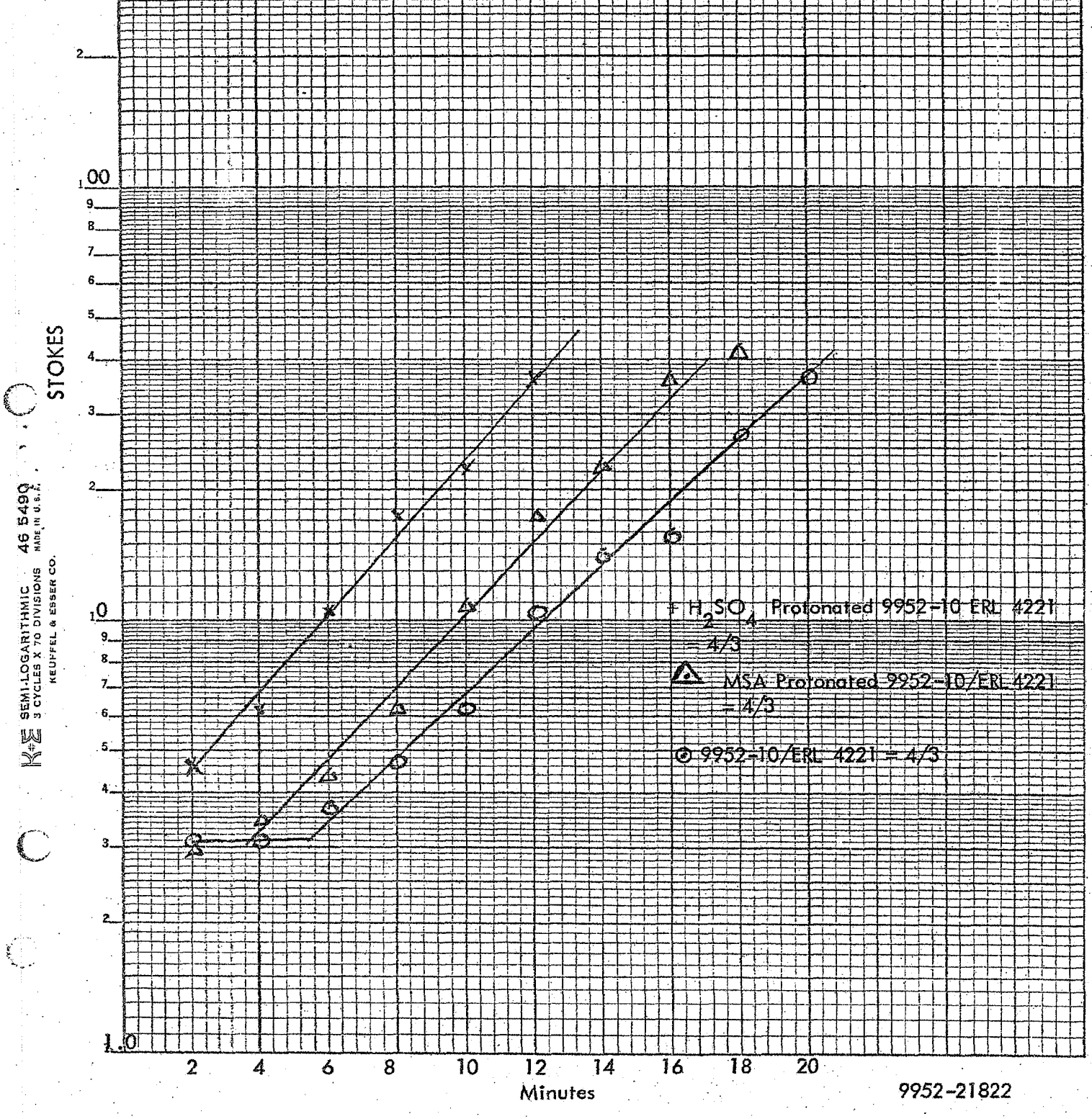
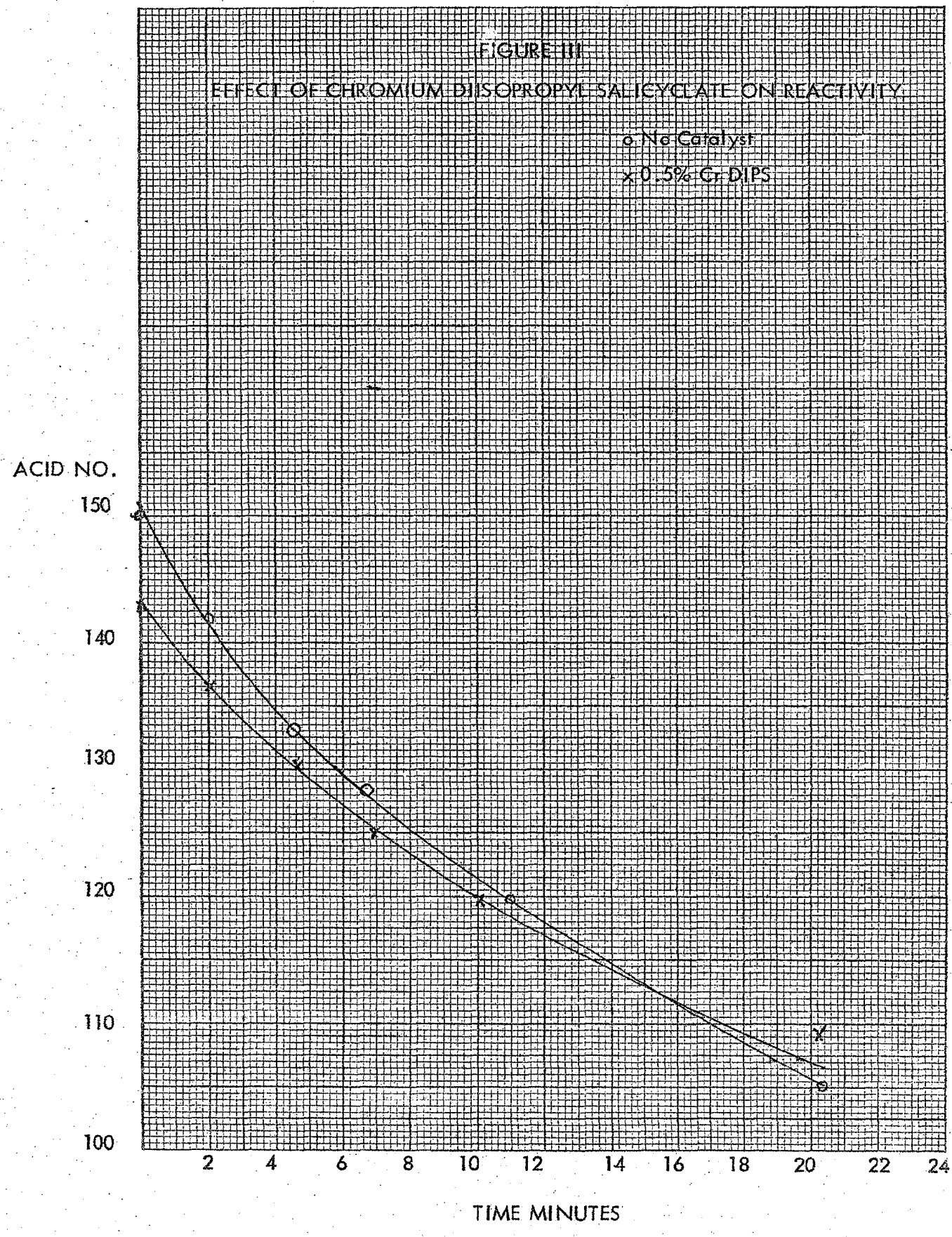


FIGURE III

EFFECT OF CHROMIUM DIISOPROPYL SALICYCLATE ON REACTIVITY

o No Catalyst

× 0.5% Cr DIPS



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2. D. Pascale, MRL Report R-60-39 (1960)
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