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SYNTHESIS OF POLYESTER FOAMING RESINS

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U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

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SYNTHESIS OF POLYESTER FOAMING RESINS

Prepared by

I. Silver and J. Parker

ABSTRACT: In accordance with a joint program established by the Naval Ordnance Laboratory and the Naval Air Development Center, this Laboratory has synthesized approximately eighty resins for consideration as foamed core materials in radomes. These resins have been forwarded to NADC for evaluation. Equations for calculating hydroxyl numbers and residual water content have been derived and their applicability discussed. The reaction of residual water in the resin with the isocyanate-resin reaction product to form urea derivatives capable of further cross-linking through active hydrogens has been considered.

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

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This report describes the polyester resins synthesized for the Naval Air Development Center in accordance with a joint program leading to the development of improved foamed core materials for radomes. This program was carried out under Task NOL-169-51 and is now considered completed. This represents a final report on the subject.

EDWARD L. WOODYARD
Captain, USN
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By direction

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SYNTHESIS OF POLYESTER FOAMING RESINS

INTRODUCTION

1. The Naval Ordnance Laboratory was requested by the Naval Air Development Center at Johnsville, Pennsylvania, to enter into a joint program leading to the development of improved polyester-diisocyanate foams for use as sandwich materials in radome structures (references a and b). The Naval Ordnance Laboratory, because of the availability of laboratory facilities undertook the synthesis of polyester resins whereas the Naval Air Development Center assumed responsibility for the evaluation of these resins as foams.

2. The polyester-diisocyanate foams were first developed by the Germans in the last war and certain basic formulations suggested by their work have been further developed by DeFell and Richardson and the Goodyear Rubber Company in this country. The latter has been mainly responsible for the development of new and improved foaming techniques (references c and d).

3. The German resin and the one currently being used by Goodyear is based on the esterification of adipic acid and phthalic anhydride with glycerol or trimethylolpropane to the consistency of a thick syrupy liquid with an acid number ranging from 20-40. Although this resin has proven capable of meeting most of the present requirements of the foam, it was believed that the potentialities in this type of material had not been fully realized and that further improvements in strength, dielectric properties and processability could be attained through alterations in the structure of the resins.

4. Since the war other mono- and polyfunctional acids and alcohols have become available in commercial and experimental quantities and consequently the synthesis of improved polyester resins appeared to be justified. Dr. H. Moore of NADC has prepared a critical review of the chemistry of the present foaming resins and has suggested two main modes of attack in improving the present foams (reference e). The first consists essentially of a screening program to modify the basic German resin formulation with polyfunctional alcohols and acids and viscosity modifiers and to determine the effect of these resin components on the viscosity, reactivity and properties of the foamed resin. A list of resin components for consideration in this program has been prepared by Dr. Moore in reference (e). The second phase consists in synthesizing unsaturated resins (Terpolymer type) which would attain maximum strength by the formation of carbon to carbon bonds through addition polymerization as well as through cross-linking with diisocyanates.

CHEMISTRY OF POLYESTER-DIISOCYANATE FOAMS

5. The chemistry of the polyester-diisocyanate foam has been described in several publications. Dr. Moore in reference (e) includes a complete bibliography on the subject. Basically a polyester containing an excess of hydroxyl and carboxyl groups reacts with a difunctional isocyanate such as tolylene diisocyanate (T.D.I.) to form urethane and amide linkages, respectively, with the simultaneous evolution of carbon dioxide. The latter is entrapped in the viscous fluid, expansion occurs and through cross-linking, the reaction mass is quickly polymerized.

6. Polyester resins are prepared by condensing polyacids and polyalcohols with the elimination of water. With difunctional acids and alcohols as reactants, the resin formed is linear. The physical properties are determined to a considerable extent by the chain length and degree of crystallinity and hydrogen bonding in the resin, the latter in turn being a function of the molecular structure of the reactants.

7. Polyester resins used in the preparation of foams, however, are synthesized from tri-functional alcohols and dibasic acids. This tri-functionality leads to chain growth in three dimensions (cross-linking) and eventual gelation of the resin where equimolecular amounts of acid and alcohol (OH/COOH mole ratio = 1.5:1) are used gelation occurs at about 75% esterification. This is undesirable from the viewpoint of processability of the foam since a liquid resin of pourable viscosity is necessary. Any increase in OH/COOH ratio results in a lower molecular weight product but avoids the tendency to gel. The German formulation is based on a OH/COOH mole ratio of 2:1 as shown below:

<u>Composition</u>	<u>Moles</u>	<u>Functionality/Mole</u>	<u>Total Functionality</u>
Adipic acid	2.5	2	5 (COOH)
Phthalic anhydride	0.5	2	1 (COOH)
Glycerol	4.0	3	12 (OH)

8. When polymerized to an acid number of 40, this resin has a viscosity of about 700 poises. Increasing the ratio (greater concentration of glycerol) results in free glycerol in the reaction product which is detrimental to the strength of resulting foam. Decreasing the ratio to below 1.5:1 would probably result in an extremely viscous and probably unusable resin at an acid number of 40. It is obvious that effecting a change in properties of the foam through variation in the OH/COOH ratio is seriously limited.

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9. By employing the German formulation as a base it is possible to vary the properties of the foam by substitution of other difunctional acids for adipic and trifunctional alcohols for glycerol. Condensing the resin to an acid number of 40 with a given viscosity is not always possible as each of the substituents used has a specific effect on the viscosity of the reaction product. Lowered viscosities may be compensated for by decreasing the OH/COOH ratio. Increases in viscosity are more difficult to control in that the use of modifying agents may be required. These agents are usually mono- or difunctional alcohols or acids which lower the viscosity by decreasing the cross-linking in the resin. This may be detrimental since softer foams usually result. Compensation for this softening effect can be made by the use of substituents contributing to the hardness and toughness of the foam. This includes aromatics (phthalic anhydride), halogenated acids (bromo-succinic), unsaturated acids (maleic) or the use of higher functionality substituents (pentaerythritol).

10. Numerous combinations of formulations are evidently possible. By systematically studying these combinations in terms of viscosity, reactivity with diisocyanates and the physical and electrical properties of the foam, it is probable that a new formulation can be developed with properties considerably superior to those of the German formulation.

EXPERIMENTAL PROCEDURES

Resin Preparation

11. A sketch of the apparatus used in carrying out the esterification is given in Figure 1. Briefly, the resins were prepared in three necked flasks heated by Glascol equipment and under an atmosphere of nitrogen. Water of reaction was condensed and measured in graduated cylinders attached to the receiver. Residual water in the resin can be removed by vacuum. The reaction was usually carried out over a period of several hours at maximum temperatures ranging from 130°C. to 250°C.

Analytical Methods

12. The analytical methods employed have been set forth in reference (f). In view of the considerable amount of time involved in analyzing the resins and the conflicting desire to increase the output of resins, calculated values were often used for water content and the hydroxyl number. Formulas were derived, which allowed calculation of these values when experimental data on acid number and the amount of water of condensation

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in the receiver was available. A summary of the analytical data and cooking schedules are given in Table 1.

13. Residual water content: The first group of resins prepared in this program (Table 2) were checked for water content by the Stark-Dean method. This method was considered least desirable for many of the resins as continued heating causes further esterification and consequently high water values. The Kari Fisher method was attempted on a small number of samples but the results were not considered reliable because of poor reproducibility and was abandoned in favor of calculated data. Further refinements in technique are probably necessary. Reference (1) discusses the derivation of the formula for calculating the water content of the resins. The final formula is given below:

$$\% \text{ H}_2\text{O} = W_p = \frac{100}{R} (W^1 - \frac{18\Delta X}{X_0})$$

$W^1 = W_e - W_d$ = residual water in resin plus water used in hydrolyzing the anhydride (gm)

$W_e = 18\Delta X$ = total theoretical water of esterification (gm)

W_d = total measured weight of distillate (gm)

$\Delta X = (X_0 - \frac{nR}{m})$ = number of mols of COOH reacted

X_0 = initial number of mols of COOH in reactants

a = initial number of mols of anhydride in reactants

n = acid number

$R = R_0 - W_d$ = weight of resin batch (gm)

R_0 = initial weight of reactants (gm)

$m = 56,100 = 10^3 \times$ the molecular weight of KOH

This calculation, however, ignores the possibility of ether formation and depends upon the accuracy of determining the weight of distillate and the estimated extent of anhydride hydrolysis. While the equation could be useful in production synthesis of a single resin type, experimental values should be determined where the resin reaction characteristics are unknown.

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14. Water values for several resins were obtained with a vacuum-oven method which is considered the most reliable of the several methods studied. Where available these values should be used in calculating required T.D.I. for foaming. Essentially, this method consists of measuring the loss of weight of a given sample in a vacuum oven (15 hrs @ 80°C.) and measuring the change in the acid #. By accounting for any water of esterification formed and assuming that no loss of non-aqueous constituents occurs, the following formula was used to calculate residual water content.

$$\% \text{ H}_2\text{O} = W_p = \left[\frac{(r_2 - r_1) - \Delta w}{r_1} \right] 100$$

where: r_1 = initial sample weight (gm)

r_2 = final sample weight (gm)

$$\Delta w = \frac{18}{m} (n_1 r_1 - n_2 r_2)$$

n_1 = initial acid number

n_2 = final acid number

m = 56,100

In some cases the correction term $\frac{\Delta w}{r_1}$ may be neglected, however, it should always be calculated where the resin reaction characteristics are unknown or where the resin is known to be far from its water-ester equilibrium. In the latter case the acid number may change considerably making the correction term appreciable.

15. Unfortunately this project was terminated before water values by the vacuum-oven method for all of the resins synthesized could be obtained. It is suggested, however, that NADC carry out such determinations on those resins which appear to be most promising.

16. Hydroxyl number: Standard acetylation techniques (reference f) were used for determining hydroxyl numbers for many of the resins tabulated in Table 1. An equation was derived (reference i) permitting the calculation of hydroxyl numbers when corresponding acid numbers were known. In order to conserve time, calculated values were later used rather than the experimental values. The following formula was employed to calculate hydroxyl numbers:

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$$h = n + \frac{m}{R} (Y_0 - X_0)$$

h = hydroxyl number

m = 56,100

R = original batch weight minus the water of distillation

Y_0 = total mols OH charged

X_0 = total mols COOH charged (including anhydride)

n = acid number

17. For many resins, the agreement between experimental and calculated values are very good; in others, the differences between experimental and calculated values are of the same order as that between experimental determinations. Further work on refinement of the standard acetylation technique appears necessary as low results are often obtained unless large excesses of acetic anhydride are used.

18. One limitation to the formula as it is used is the possible reduction of hydroxyl number through etherification. This reaction is difficult to measure and thus is not considered in the formula. No corresponding change in acid number occurs with the loss of OH - groups in the formation of an ether. In view of this fact, direct experimental determinations are considered more reliable than calculated values unless it is known that no ethers are formed during the resin synthesis.

19. Total reactivity including water content: In view of the analysis made by C. Beyer and coworkers (reference g) of network formation for polyester-diisocyanate elastomers ("vulcollans"), the water content of the polyester to be used for foaming should be considered in the calculation of theoretical quantities of tolylene diisocyanate (T.D.I.) (reference j).

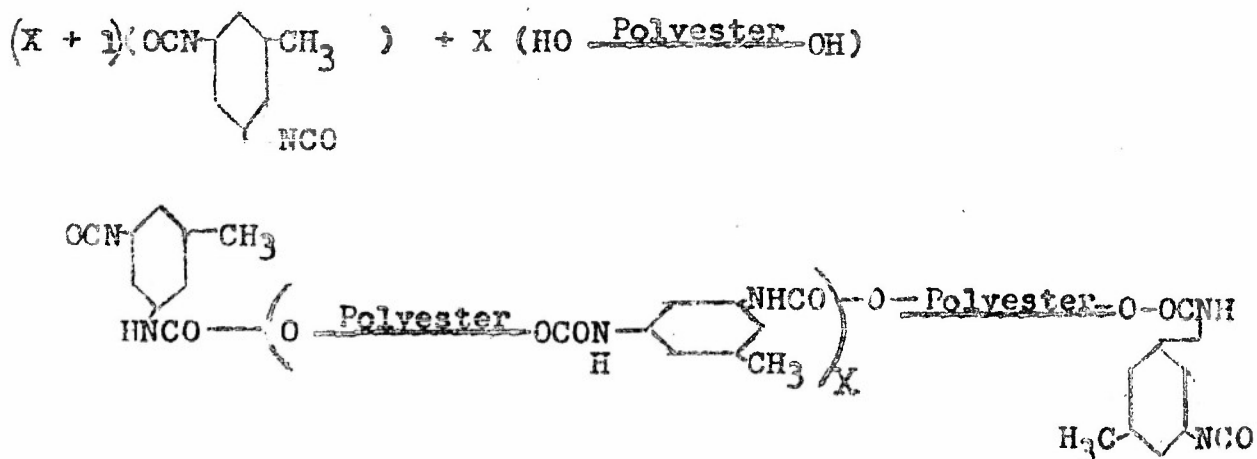
20. Previous calculations based on the assumption that one-half or one molecule of T.D.I. was required for reaction with one molecule of water gave results indicating that the T.D.I. required for reaction with the water in the polyester was negligible. The considerable excesses of T.D.I. needed for optimum results in the cases of many of the polyesters seemed to have some relationship with the water content.

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21. Recalculations based on the 3:2 T.D.I. to water ratio showed that the amount of T.D.I. previously thought to be excess was in many cases less than theoretical.

22. Following Beyer's reasoning the following reaction scheme is set up:

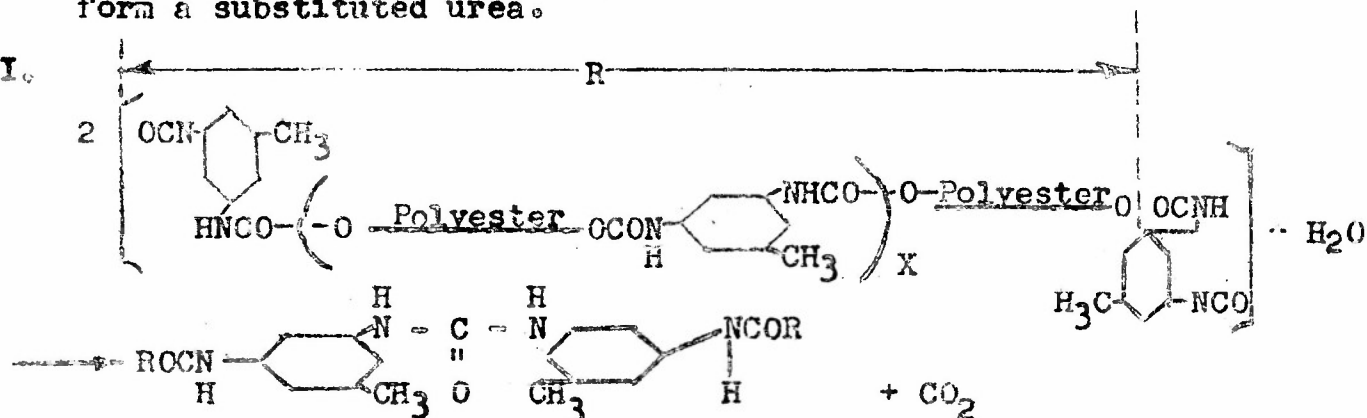
I.



23. This reaction emphasizes the possible evils of too great an excess of T.D.I., particularly where there is little cross-linking in the polyester. A 1:1 ratio of T.D.I. to polyester functional groups would result (theoretically) in only one polyester unit per molecule. It seems likely that a ratio somewhere between 1:1 and 1:2 T.D.I. to polyester functional groups would be optimum since it is desirable that the product of (I) end with a T.D.I. molecule. For present purposes of calculation the 1:2 ratio is chosen for maximum chain length.

24. The product of I is capable of reaction with water to form a substituted urea.

II.



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25. The reaction product of II possesses two active hydrogens at the urea bridge (arrows) which may react further with isocyanate increasing the cross-linking.

26. In the above reaction scheme it can be seen that 3/2 to 2 mols of T.D.I. are required for one mole of water.

27. If all of the polyester functional groups may be considered to react equally with the T.D.I. the total number of mols of reactants (polyester functional groups plus water) will be

$$\left(\frac{n + h}{56,100} + \frac{W_p}{1800} \right) g$$

n = acid number

h = hydroxyl number

g = grams polyester

W_p = percent residual water

28. The first term is the number of mols of polyester functional groups, the second, the mols of water in the polyester.

29. From reaction I the ratio 1:2 for mols T.D.I. per mol of polyester functional groups was chosen. For the mols T.D.I. per mol water the ratio 3:2 was chosen, since only one of the urea bridge hydrogens readily reacts which is analogous to similar reactions of T.D.I. and substituted ureas (reference g).

30. The theoretical weight of T.D.I. per gram of polyester is then:

$$\left[\frac{1}{2} \left(\frac{n + h}{56,100} \right) + \frac{3}{2} \frac{W_p}{1800} \right] 174$$

(MW of T.D.I. = 174)

or

$$\frac{\text{gms. T.D.I.}}{\text{gms. Polyester}} = 1.55 \frac{(n + h)}{1000} + 0.145 W_p$$

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31. This calculation has been carried out for most of the resins sent to the Naval Air Development Center and the results tabulated in reference (j). Wherever there is some question of the proper water content, new values should be obtained for the above formulation. It is also necessary to call attention to the fact that acid numbers may be expected to change on storage of the resin as it tends to reach a state of equilibrium. Wherever resins have been stored for long periods of time, it may be worthwhile redetermining acid numbers and water contents.

DISCUSSION

32. Approximately eighty resins were forwarded to NADC for evaluation. These resins, along with data on their acid and hydroxyl numbers and residual water content are listed in Tables 1-6. A considerable number of other resins were attempted but either due to the incompatibility of the reactants or to the formation of gels or solids, they are not considered worthwhile reporting.

33. In the initial phase of this program, a wide range of resin compositions was attempted in accordance with a projected line of attack agreed to by NADC and NOL (references b and h). It was planned to prepare each resin in 2 acid numbers, 40 and 60, and if possible within a viscosity range of 600-700 poises. These resins are tabulated in Table 2. It was found, however, that with variations in OH/COOH ratio and in concentration and type of reactant, the resulting viscosities often varied in an unpredictable manner. By the use of viscosity modifiers (di- and mono-functional constituents, viscosities were subject to closer control but usually at some sacrifice in available cross-linking groups.

34. Resins in Table 4 were synthesized mainly with the idea of studying the effect of reducing the hydroxyl number through the use of monofunctional substitutes on the viscosity of the resin and on the physical properties of the foam. The theory had been stated (reference e) that due to rapid gelation and resulting steric hindrance not all of the OH groups react with the T.D.I. in the foaming of the standard German or Goodyear resin. It was assumed that using modified formulations a reduction in hydroxyl number could be possible without effectively decreasing the degree of cross-linking through reactive OH groups. Such a reduction in OH number could result in lowered water absorption and improved dielectric properties provided all of the available OH groups would react with T.D.I.

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35. Resin IB-1b contained acrylic acid as a monofunctional substitute. This approach should prove to be promising as it suggests a means of preparing formulations with reduced OH number. These resins would require less diisocyanate and yet attain the proper degree of cross-linking through addition polymerization of the acrylic constituent.

36. Table 5 lists resins prepared with trifunctional acids and difunctional alcohols. These reactants are used in some resins in such concentrations that the mol ratio of hydroxyl to carboxyl is the inverse of that of the standard German resin without a change in the overall number of available reactive groups ($n + h$). Because of the high acid number, exceedingly low density foams should be possible with this class of resins and consequently provide a method for adjusting the density of foams without resorting to the use of diluents such as water or acetone and possible degradation of physical properties.

37. Table 3 represents further variations in the standard German formulation employing additional difunctional acids and alcohols. Attempts were made to substitute terephthalic acid directly for the phthalic anhydride but no easy esterification of the acid was obtained. It was necessary to esterify the terephthalic acid in an excess of diethylene glycol and to add the reaction product to glycerol and adipic acid and continue the reaction. This accounts for the low viscosities of resins containing terephthalic acid. These resins can be considerably improved by developing a method for esterifying the acid with glycerol without the use of diethylene glycol. Further work along these lines should be carried out as terephthalates may conceivably contribute greater strength and a higher heat distortion point than the phthalic anhydride (reference k).

38. Resins in the "D" series in Table 6 were formed by condensing hydroxy dibasic acids with difunctional alcohols. The aim of this series was to prepare linear chains with periodically spaced hydroxyl groups available for cross-linking with T.D.I. By varying the position and number of OH groups in the chain, it should be possible to vary the rate of the reaction with T.D.I. and to control the pour point viscosity more closely. Actually the OH groups enter into reaction with the hydroxy acids and the concept of controlled spacing of the OH group is difficult to achieve.

39. Resins formulated with pentaerythritol are listed in Table 6. As a polyfunctional alcohol it has found considerable

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use in alkyd vehicles for varnishes by contributing toughness and hardness. By analogy, the use of pentaerythritol could conceivably result in foams with increased strength. In practice the tetrafunctionality of the pentaerythritol results in rapid gelation and considerable difficulty was experienced in preparing resins with both the proper acid number and viscosity. Modifying agents with difunctionality were used to yield resins with satisfactory viscosities possibly offsetting any advantage derived from the pentaerythritol. Additional formulations should be considered aiming towards incorporating the maximum amount of pentaerythritol in the resin.

40. The synthesis of unsaturated foaming resins formed the second major portion of this program. Unfortunately, only a small number of resins were attempted and of these only three were sent to NADC. This type of resin would be desirable in that it offers a method by which large reductions in the use of T.D.I. would be possible without loss of cross-linking. For example, unsaturated resins with low acid numbers and hydroxyl numbers could be reacted with T.D.I. The hydroxyl number should be the minimum required to cause sufficient thickening of the resin to retain the gas as it is formed. Subsequent hardening and development of strength properties can be attained through additional polymerization of the unsaturated bonds.

41. Due to the linearity of these resins it becomes necessary to employ cross-linking agents (styrene, diallyl phthalate, etc) in order to obtain any degree of satisfactory strength and, also to thin the resin to a suitable viscosity. The choice of type and amount of cross-linking agent should be studied simultaneously with the synthesis of these resins. Compatibility of the cross-linking agent must be considered and modification of the resin may be necessary to improve compatibility. In addition the catalytic system used to polymerize the resin must be considered in developing a technique for foaming these resins. Resin IIA-12 is a simple equimolecular combination of difunctional alcohols and acids including maleic anhydride condensed to acid and hydroxyl numbers of about 40. Resins are closer to the standard German formulation in that trifunctional alcohols are employed and the reaction product has a high hydroxyl number. Hydroquinone was used in IIA-9 to impart possible toughness to the foam and to improve the compatibility of the resin with styrene.

CONCLUSIONS AND RECOMMENDATIONS

42. Approximately 80 resins representing several basic types were synthesized and forwarded to NADC for use as foaming materials in radomes.

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43. Formulas were derived to obtain approximate values of the hydroxyl number and water content. In view of the errors inherent in these calculations, it is suggested that direct experimental procedures be employed to obtain these data when the nature of the reactions is unknown.

44. The importance of water content in calculating the required T.D.I. for reaction was pointed out and an equation derived for this purpose.

45. It is recommended that in the future an integrated program of resin synthesis and evaluation be organized under the direct responsibility of a single group. The progress of the program is dependent to a considerable extent on results obtained in the evaluation of the resins. Separation of these two functions as in the present program results in delays and prevents proper planning.

Table 1 Analytical Data and Cooking Schedules

Resin	Starting Date Cooking	Maximum Temp. °C.	Hours in 100°-140° °C. temp. range	Final Cooking Acid No.	Final Acid # at shipping	Stark-Dean	% Water Content		Hydroxyl Number		Shipping Date	Note	
							Karl Fisher	Vacuum	Calculated	Exp.			Calculated
I-1	6/21/50	210	2	65.3	61.7	1.8	-	0.60	448.8	531.9	Aug. 1950		
I-2	6/30/50	205	4	42.9	42.90	1.7	-	0.84	396.8	513.1	"		
II-1	6/19/50	185	6-1/4	67.1	65.0	2.0	-	0.66	500.1	494.8	"	P-toluene sulfonic acid, .3 gm	
II-2	6/26/50	210	4-1/4	46.2	46.2	1.7	-	-	463.5	478.2	"		
II-2a	5/25/51	201	5	44.6	39.1	0.3	-	0.44	-	437.4	July 1951		
III-1	10/15/50	143	4	63.2	65.70	1.4	-	0.70	430.0	434.7	Aug. 1950		
III-2	6/27/50	200	2	41.1	40.6	1.7	-	1.22	474.6	414.8	"		
IV-1	7/19/50	170	3	66.4	62.9	2.0	-	1.81	357.9	400.2	"		
IV-2	6/27/50	165	5-1/2	46.1	46.5	1.2	-	0.61	278.6	378.2	"		
V-1	7/5/50	165	4-1/4	67.9	65.9	2.4	-	0.04	398.9	385.3	"		
V-2	7/5/50	165	5	43.0	43.0	1.9	-	0.00	387.7	-	"		
V-1,2	6/30/50	175	6	23.8	25.8	1.7	-	-	-	351.1	Sept. 1951		
VI-1	7/6/50	180	7-1/4	66.2	66.0	1.7	-	-	437.9	479.0	Aug. 1950		
VI-2	7/21/50	210	3-1/4	46.1	46.1	1.1	-	-	426.5	485.2	"		
VII-1	7/26/50	160	6-1/2	60.5	60.0	0.6	-	-	301.3	310.2	Oct. 1950		
VII-2	7/26/50	160	8-1/4	46.8	44.7	0.4	-	-	275.4	-	"		
VIII-1	8/24/50	172	8	65.7	65.1	0.9	-	-	344.7	421.1	"		
VIII-2	8/24/50	173	10-3/4	40.1	40.4	0.5	-	0.32	324.7	-	"		
IX-1	10/4/50	138	4	53.4	56.3	-	-	1.23	268.8	-	Apr. 1951	Acid No. reversed	
IX-2	10/4/50	165	6-1/2	41.7	40.6	0.4	-	0.23	300.3	393.4	"	"	
XII-1	8/30/50	187	6	63.9	65.3	1.1	-	-	365.5	474.9	Oct. 1950		
XII-2	8/30/50	187	10	45.5	46.7	3.5	-	-	369.6	-	"	Acid No. reversed	
XV-1	8/31/50	181	16	66.8	64.4	3.8	-	-	425.1	-	"	"	
XV-2	8/31/50	181	20	40.8	42.3	-	-	-	415.1	-	"	"	
XVI-1	8/28/50	170	4	59.3	60.6	-	-	-	337.1	-	"	"	
XVI-2	8/28/50	170	5	45.4	44.6	2.2	-	-	386.1	-	"	"	
XVII-1	9/6/50	163	6	64.4	61.4	5.3	-	-	298.8	-	"	"	
XVII-2	9/6/50	178	6-1/2	40.9	49.2	4.2	-	-	314.6	-	"	"	
XVIII-1	8/16/50	174	10	65.4	64.5	2.7	-	0.64	315.4	472.8	"	"	
XVIII-2	8/16/50	180	11-1/2	44.9	45.5	0.9	-	0.39	420.7	-	"	"	
XIX-1	8/17/50	184	8	66.1	68.9	0.8	-	-	325.6	384.6	"		
XIX-2	8/17/50	184	3-1/4	47.4	45.1	0.8	-	-	265.1	-	"		
XXI-1	9/21/50	176	8	59.0	60.0	2.4	-	-	426.3	435.8	"	Acid No. reversed	
XXI-2	10/23/50	250	7	40.0	34.2	-	-	-	414.0	469.3	Apr. 1951		
XXV-2	10/22/50	250	4-1/2	51.1	50.8	-	0.61	-	365.6	432.7	"		
XXV-3	6/8/51	177	3	55.2	55.2	0.4	-	-	-	345.7	July 1951		
IA-10	6/5/51	190	16	38.5	38.3	-	-	2.17	0.2	-	360.7	"	
IA-11	6/14/51	170	12	47.3	47.3	-	-	0.4	-	-	-	Sept. 1951	
IA-13	6/21/51	170	19	94.5	110.1	1.9	-	-	-	-	454.7	"	
IA-14	6/21/51	200	10-1/2	53.5	53.5	-	-	0.83	0.0	-	504.6	"	
IA-16	9/11/51	193	12	38.2	39.6	-	-	-	0.3	-	401.1	Oct. 1951	
IA-20	7/12/51	170	2-1/2	43.4	43.9	-	-	0.70	0.4	-	447.8	Sept. 1951	
IA-21	7/13/51	220	3-1/4	22.5	22.5	-	-	-	0.1	-	365.2	"	

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Table 1 (continued)

Resin	Starting Date Cooking	Maximum Temp. °C.	Hours in 100°-Max. %C. temp. range	Final Cooking Acid No.	Final Acid # at shipping	Stark-Dean	% Water Karl Fischer	Content Thomas	Calculated	Hydroqyl Number Exp.	Calculated	Shipping Date	Note
IA-22	7/13/51	180	25-1/2	40.1	40.1	"	"	"	0.4	"	381.4	Sept. 1951	
IA-23	7/17/51	230	20	28.3	28.3	"	"	"	0.2	"	326.0	"	
IA-24	7/18/51	205	24-1/2	29.1	29.1	"	"	"	0.8	"	353.5	"	
IA-27	8/2/51	190	9	36.1	36.1	"	"	0.61	0.0	"	450.6	"	
IA-28	8/22/51	193	8-3/4	34.5	34.5	"	"	"	0.7	"	347.0	Oct. 1951	
IA-29	8/21/51	180	13-1/2	34.9	34.9	"	"	"	0.9	"	379.2	"	
IA-30	8/21/51	175	18-1/2	49.6	49.6	"	"	0.14	"	"	437.5	Sept. 1951	
IA-31	6/28/51	145	8-3/4	48.9	48.9	"	"	"	1.4	"	417.0	"	
IA-32	6/29/51	155	11	52.5	52.5	"	"	0.46	2.1	"	399.3	"	
IA-33	6/30/51	210	10	11.8	10.1	"	"	"	0.3	"	392.1	"	
IA-33a	6/30/51	205	10	29.6	29.6	"	"	"	0.3	"	419.7	"	
IA-34	6/30/51	160	5	49.9	49.9	"	"	"	0.9	"	421.6	"	
IA-35	8/2/51	195	15	30.9	30.9	"	"	"	3.6	"	421.0	Oct. 1951	
IB-1	10/25/50	209	8	25.0	23.5	0.6	"	0.27	0.0	316.3	325.0	Apr. 1951	
IB-1a	9/10/51	210	8-1/2	37.1	"	"	"	"	0.0	"	325.3	Oct. 1951	
IB-3	11/9/50	185	10	41.2	47.8	0.7	"	"	"	352.0	"	Apr. 1951	
IB-12	11/23/50	163	4	41.3	42.2	0.1	"	"	"	399.0	"	"	Acid No. reversed
IB-13	11/28/50	159	17	41.1	50.5	0.6	"	"	"	256.3	"	"	
IB-14	12/21/50	165	5	49.3	50.3	0.9	"	"	"	290.7	"	"	
IB-15	12/21/50	246	3-3/4	34.6	35.6	0.6	"	"	"	228.4	"	"	
IB-16a	2/16/51	225	5	47.7	55.4	0.4	"	"	"	356.6	"	"	0.5 gm hydroquinone 0.5% m-cresol
IB-17	1/25/51	147	13	50.2	52.0	0.4	"	"	"	231.3	281.6	"	
IC-10	11/10/50	260	25	45.4	54.3	"	"	"	4.9	"	16.1	Oct. 1951	
IC-16	3/20/51	170	5	395.2	395.9	"	"	"	0.6	"	163.8	"	
IC-19	4/16/51	130	2-1/2	254.6	254.6	"	"	1.7	1.3	"	254.6	July 1951	
IC-30	8/17/51	210	21	142.5	142.5	"	"	"	0.4	"	45.9	Oct. 1951	
IC-31	9/11/51	130	4-1/2	247.1	245.8	"	"	"	3.8	"	245.8	"	
ID-5	4/19/51	160	6	22.7	22.7	"	"	"	2.6	"	245.7	July 1951	Residual H2O vacuum removed during last hour
ID-6	4/19/51	168	13.5	52.8	52.8	"	"	"	0.2	"	240.2	"	
ID-7	5/24/51	168	13	42.3	42.3	"	"	"	1.1	"	299.8	"	
IE-2	6/5/51	165	12	61.5	61.5	"	"	"	1.4	"	298.6	"	
IE-4	3/20/51	174	13	27.3	27.3	"	"	"	0.3	"	349.8	"	
IE-5	6/20/51	210	23-1/2	29.6	30.6	"	"	"	1.5	"	339.1	Sept. 1951	
IIA-9	8/23/51	165	15-1/2	69.2	69.2	"	"	"	1.1	"	509.0	Oct. 1951	
IIA-12	10/25/50	246	8-1/2	43.4	45.5	"	"	0.46	"	"	40.6	"	
IIA-13	8/21/51	185	9	22.2	25.0	"	"	0.12	0.0	"	471.7	"	
IIIA-1	8/2/51	140	15-1/2	41.2	42.3	"	"	"	0.02	"	493.2	"	
IIIA-2	8/23/51	172	2	42.8	42.8	"	"	0.52	0.0	"	491.4	"	
IIIB-1	8/2/51	193	12-3/4	4.9	4.9	"	"	1.16	0.0	"	435.3	Sept. 1951	

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Table 2
 Resin Compositions

Composition ^a	I-1	I-2	II-1	II-2	II-2a	III-1	III-2	IV-1	IV-2
Adipic acid	2.5	2.5	2.5	2.5	2.0	2.5	2.5	2.5	2.5
Phthalic anhydride	0.5	0.5	0.5	0.5	0.4	0.5	0.5	0.5	0.5
Glycerol	4.0	4.0	3.8	3.8	2.6	-	-	-	-
Trimethylolpropane	-	-	-	-	-	4.0	4.0	3.8	3.8
1,4 Butanediol	-	-	-	-	0.4	-	-	-	-
OH/COOH (mole ratio)	2:1	2:1	1.9:1	1.9:1	1.8:1	2:1	2:1	1.9:1	1.9:1
Viscosity (poises)	655	658	245	730	>1000	1000	>1000	725	>1000
Acid %	61.7	42.9	65.0	46.2	39.1	65.7	40.6	62.5	46.5
	V-1	V-2	VI-1	VI-2	VII-1	VII-2	VIII-1	VIII-2	
Adipic acid	2.5	2.5	2.25	2.25	2.5	2.5	2.25	2.25	
phthalic anhydride	0.5	0.5	0.75	0.75	0.5	0.5	0.75	0.75	
Glycerol	-	-	3.8	3.8	-	-	-	-	
Triethanolamine	3.8	3.6	-	-	-	-	-	-	
Triisopropanolamine	-	-	-	-	3.6	3.6	-	-	
1,2,6 Hexanetriol	-	-	-	-	-	-	3.8	3.8	
OH/COOH (mole ratio)	1.9:1	1.9:1	1.9:1	1.9:1	1.8:1	1.8:1	1.9:1	1.9:1	
Viscosity (poises)	585	665	>1000	>1000	>1000	>1000	435	>1000	
Acid %	65.9	43.0	66.0	46.1	60.0	44.7	65.1	40.4	
	IX-1	IX-2	XII-1	XII-2	XV-1	XV-2			
Adipic acid	1.5	1.5	3.0	3.0	5.0	5.0			
Phthalic anhydride	1.5	1.5	3.0	3.0	-	-			
Carbic anhydride	-	-	-	-	1.0	1.0			
Glycerol	-	-	6.0	6.0	7.6	7.6			
1,2,6 Hexanetriol	3.8	3.8	-	-	-	-			
1,3 Butanediol	-	-	2.0	2.0	-	-			
OH/COOH (mole ratio)	1.9:1	1.9:1	1.8:1	1.8:1	1.9:1	1.9:1			
Viscosity (poises)	>1000	>1000	>1000	412	>1000	>1000			
Acid %	56.3	40.6	65.3	46.7	64.4	42.3			

^a-mole concentrations

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Table 2 (continued)

Composition ^a	XVI-1	XVI-2	XVII-1	XVII-2	XVIII-1	XVIII-2	XIX-1	XIX-2
Adipic acid	5.0	5.0	3.0	3.0	-	-	-	-
Phthalic anhydride	-	-	-	-	3.0	3.0	3.0	3.0
Sebacic acid	-	-	-	-	3.0	3.0	3.0	3.0
Tetrachlorophthalic anhydride	1.13	1.13	3.0	3.0	-	-	-	-
Glycerol	7.6	7.6	6.0	6.0	8.0	8.0	-	-
Triethanolamine	-	-	-	-	-	-	8.0	8.0
1,3 Butanediol	-	-	2.0	2.0	-	-	-	-
OH/COOH (mole ratio)	1.8:1	1.8:1	1.8:1	1.8:1	2:1	2:1	2:1	2:1
Viscosity (poises)	815	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Acid %	60.6	44.6	64.4	49.2	64.5	45.5	68.9	45.1

	XXII-1	XXII-2	XXV-2	XXV-3
Adipic acid	4.0	4.0	3.0	3.0
Phthalic anhydride	1.0	1.0	-	-
Tetrachlorophthalic anhydride	-	-	3.0	4.0
Maleic anhydride	1.0	1.0	-	-
Glycerol	7.6	7.6	6.0	6.0
1,3 Butanediol	-	-	4.0	-
1,4 Butanediol	-	-	-	4.0
OH/COOH (mole ratio)	1.9:1	1.9:1	2.2:1	1.9:1
Viscosity (poises)	>1000	>1000	545	-
Acid %	60.0	34.2	50.8	53.2

^a-mole concentrations

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Table 3 Resin Compositions

Composition ^a	1A-10	1A-11	1A-13	1A-14	1A-16	1A-20	1A-21	1A-22
Adipic acid	5.0	3.0	-	-	5.0	5.0	5.0	5.0
Terephthalic acid	1.0	-	-	-	1.0	-	-	1.0
Phthalic anhydride	-	-	1.0	1.0	-	1.0	1.0	-
Tetrachlorophthalic anhydride	-	-	-	-	3.0	-	-	-
Diglycolic acid	-	-	6.0	6.0	-	-	-	-
Trifluoroacetic acid	-	-	2.0	-	-	-	-	-
Dibromosuccinic acid	-	1.0	-	-	-	-	-	-
1,4 Butanediol	-	2.0	4.0	3.0	-	-	-	-
Diethylene glycol	3.0	-	-	-	3.0	3.0	3.0	3.0
Glycerol	5.0	3.5	7.0	7.0	8.0	5.6	-	-
Trimethylolpropane	-	-	-	-	-	-	5.6	-
1,2,6 Hexanetriol	-	-	-	-	-	-	-	5.6
OH/COOH (mole ratio)	1.8:1	1.8:1	1.8:1	1.9:1	1.7:1	1.9:1	1.9:1	1.9:1
Viscosity (poises)	49	426	>1000	-	>1000	85	268	66
Acid #	38.3	47.3	110.1	53.5	38.2	43.9	22.6	40.1
	• 1A-23	1A-24	1A-27	1A-28	1A-29	1A-30	1A-31	1A-32
Adipic acid	5.0	5.0	5.0	5.0	5.0	-	-	-
Terephthalic acid	1.0	1.0	-	-	-	-	-	-
Succinic anhydride	-	-	-	-	-	5.0	5.0	5.0
Phthalic anhydride	-	-	1.0	1.0	1.0	1.0	1.0	1.0
Ethylene glycol	-	-	-	-	-	3.0	-	-
Diethylene glycol	3.0	3.0	2.0	2.0	1.0	-	3.0	3.0
Glycerol	-	-	6.3	-	-	-	-	-
Trimethylolpropane	-	-	-	6.9	6.9	-	5.6	-
Triethanolamine	-	5.6	-	-	-	5.6	-	5.6
Triisopropanolamine	5.6	-	-	-	-	-	-	-
OH/COOH (mole ratio)	1.9:1	1.9:1	1.9:1	2:1	1.9:1	1.9:1	1.9:1	1.9:1
Viscosity (poises)	545	136	216	300	>1000	>1000	436	309
Acid #	28.3	29.1	36.1	34.5	34.9	49.6	48.9	52.5

a-mole concentrations

Table 3 (continued)

Composition ^a	1A-33a	1A-34	1A-35
Succinic anhydride	5.0	5.0	5.0
Phthalic anhydride	1.0	1.0	1.0
1,4 Butanediol	-	3.0	3.0
Trimethylolpropane	5.6	-	5.6
Triisopropanolamine	-	5.6	-
Ethylene Glycol	3.0	-	-
OH/COOH (mole ratio)	1.9:1	1.9:1	1.9:1
Viscosity (poises)	>1000	320	>1000
Acid #	29.6	49.9	30.9

Table 4

Resin Compositions

Composition ^a	1B-1	1B-3	1B-12	1B-13	1B-14	1B-15	1B-16	1B-17
Adipic acid	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Phthalic anhydride	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Oleic acid	-	-	-	-	-	-	-	-
Caprylic acid	-	2.0	3.0	4.0	2.0	-	-	2.0
Lauric acid	-	-	-	-	-	2.0	-	-
Acrylic acid	-	-	-	-	-	-	2.0	-
Glycerol	8.0	8.0	-	-	-	-	-	-
Trimethylolpropane	-	-	8.0	-	8.0	8.0	8.0	-
Triisopropanolamine	-	-	-	8.0	-	-	-	8.0
OH/COOH (mole ratio)	1.7:1	1.7:1	1.6:1	1.5:1	1.7:1	1.7:1	1.7:1	1.7:1
Viscosity (poises)	764	206	216	549	337	320	>1000	>1000
Acid #	28.5	47.8	42.2	50.5	50.5	35.6	35.4	52.0

a-mole concentrations

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Table 5 Resin Compositions

Composition ^a	1C-10	1C-16	1C-19	1C-30	1C-31
Adipic acid	4.0				3.0
Azelaic acid			3.0	4.0	
Citric acid		6.0			
Evan acid ^b			3.0	4.0	3.0
Maleo-Pinaric acid	1.0				
Caproic acid		3.0			
Phthalic anhydride			0.5		0.5
Terephthalic acid				1.0	
Glycerol			4.0		4.0
Diethylene glycol	4.8			3.0	
1,4 Butanediol		4.0	2.0	6.0	2.0
2-Octanol	0.4				
OH/COOH (mole ratio)	0.9:1	0.7:1	1:1	0.8:1	1:1
Viscosity (poises)	310	>1000	443	920	510
Acid #	54.3	395.9	254.6	142.5	245.8

a-mole concentration

b-carboxy-methyl mercapto succinic acid

Table 6 Resin Compositions

Composition ^a	1D-5	1D-6	1D-7	1E-2	1E-4	1E-5
Adipic acid	-	-		2.0	7.0	-
Azelaic acid	3.0	-	1.5	-	-	3.75
Malic acid	6.0	1.0	8.0	-	-	-
1,4 Butanediol	10.0	1.0	10.0	1.0	6.0	4.0
Pentaerythritol	-	-	-	1.0	3.0	-
Sorbitol	-	-	-	-	-	1.5
Caprylic acid	-	-	-	-	-	1.5
OH/COOH (mole ratio)	2.2:1	1.5:1	1.5:1	1.5:1	1.7:1	1.9:1
Viscosity (poises)	92	>1000	>1000	>1000	126	46
Acid #	22.7	52.8	42.3	61.5	27.3	20.6

a-mole concentrations

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Table 6 (continued)

Composition ^a	IIA-9	IIA-12	IIA-13	IIIA-1	IIIA-2	IIIB-1
Adipic acid	-	-	2.0	6.0	6.0	6.0
Maleic anhydride	6.0	6.4	-	-	-	-
Phthalic anhydride	-	1.6	2.0	-	-	-
Terephthalic acid	1.0	-	-	-	-	-
Fumaric acid	-	-	3.0	-	-	-
Monoethanolamine	-	-	-	-	-	3.0
Diethanolamine	-	-	-	4.0	4.0	-
Ethylene glycol	-	-	-	3.0	1.0	4.0
1,4 Butanediol	3.0	-	-	-	-	-
Diethylene glycol	1.0	8.0	2.0	-	-	-
Glycerol	4.0	-	6.3	2.0	3.0	2.0
Hydroquinone	2.0	-	-	-	-	-
OH/COOH (mole ratio)	2:1	1:1	1.9:1	2:1	1.5:1	1.3:1
Viscosity (poises)	157	-	>1000	470	>1000	144
Acid #	69.2	40.6	26.0	42.3	42.6	4.9

a-mole concentrations

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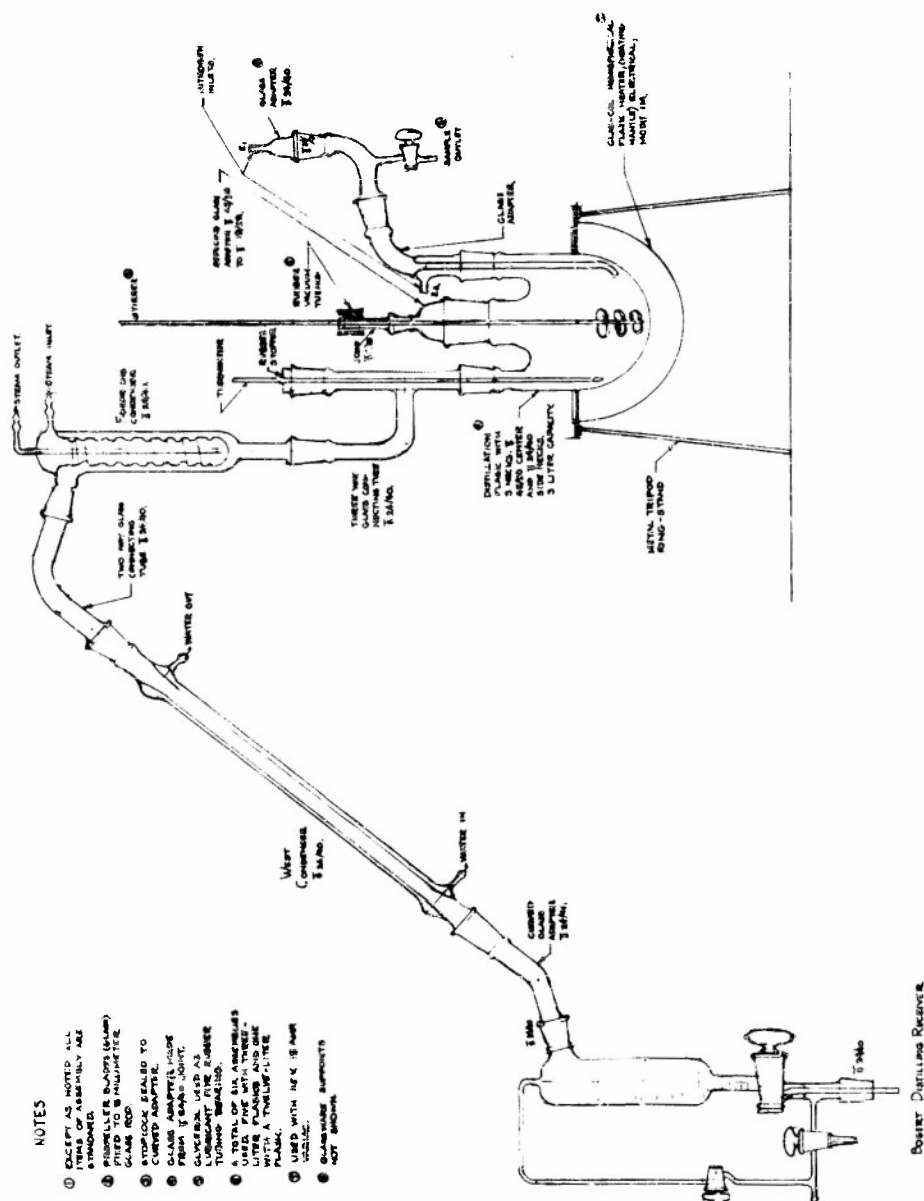


FIG. 1
APPARATUS USED IN THE SYNTHESIS OF POLYESTER RESINS