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Polymers from the Unsaturated Bisacetals of Pentaerythritol

FRANK BROWN, DONALD E. HUDGIN, RAYMOND J. KRAY
Celanese Corp. of America, Summit Research Laboratories, Summit, N. J.

Pentaerythritol is finding many new uses as a raw material in resins (*1, 4*). Some of the interesting thermosetting resins developed recently have been prepared from pentaerythritol or other polyhydroxy compounds and acrolein. Rothrock (*7*) prepared air drying coatings by a reaction of polyhydroxy compounds with unsaturated aldehydes like acrolein in the presence of strong acid catalysts. Schulz and Wagner (*9, 10, 12*) described a poly(methyl methacrylate)-like resin having good mechanical properties prepared by condensing pentaerythritol with acrolein and removing the water of acetalization. By using milder catalysts and lower reaction temperatures (*10*), they were able to isolate the unsaturated bisacetal of pentaerythritol in this condensation. In all of this initial work, the resins were obtained in one stage by introducing stoichiometric quantities of the two reactants and distilling off the by-product water without isolating the intermediate compounds.

Orth (*5, 6*) demonstrated the advantages of carrying out these reactions in two stages. In the first stage the unsaturated bisacetal of pentaerythritol was prepared and in the second stage this acetal was polymerized with a polyhydroxy compound to give the resin. If the acetalization and poly addition were run in two steps the following advantages were claimed.

Two polyhydroxy compounds of different reactivity could be used; the slower reacting compound could be fully reacted in the first stage before introducing the faster reacting compound in the second stage.

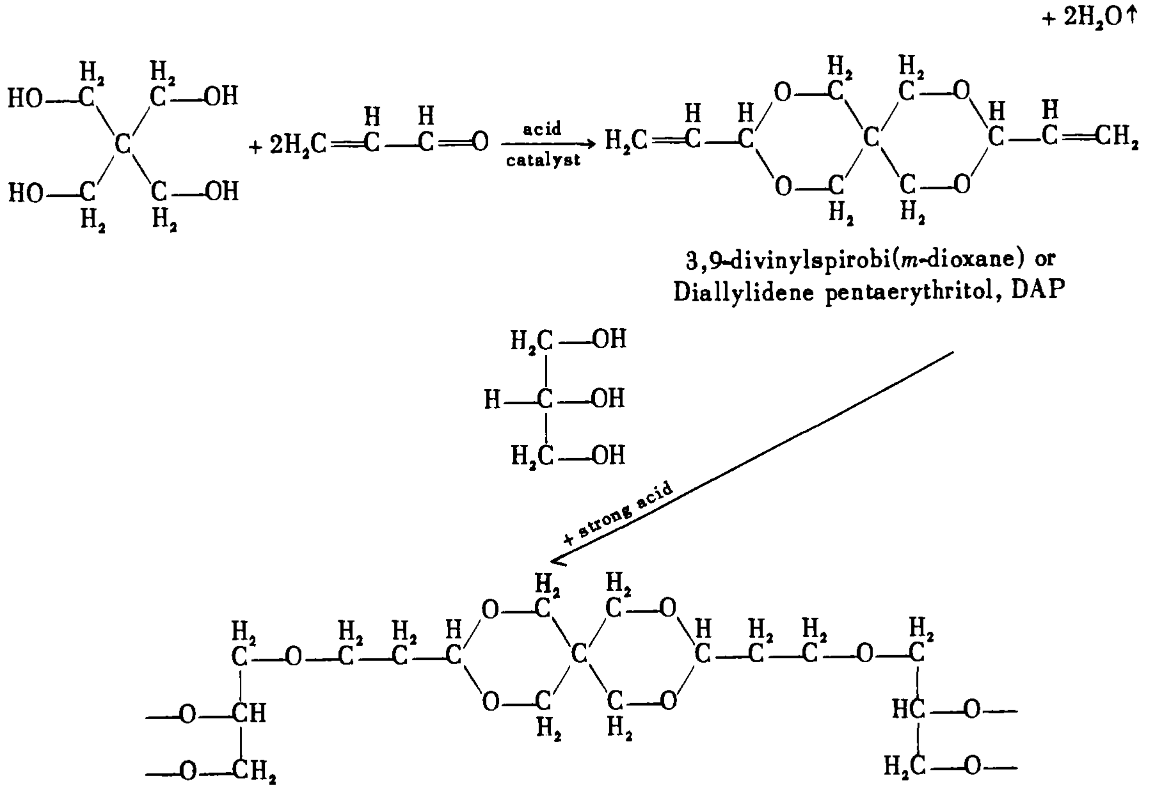
Lower shrinkage would occur on curing the resin.

Reduced water absorption of the resin would take place.

Mechanical properties of the resin would be improved.

Raw materials of technical quality could be employed in the first stage without affecting the yield, and the product of the first stage could be readily purified.

The general equation for the formation of the resin by the two-stage process is shown below.



3,9-divinylspirobi(*m*-dioxane) or Diallylidene pentaerythritol, DAP

One mole of pentaerythritol and two moles of acrolein are condensed to form the unsaturated bisacetal, 3,9-divinylspirobi-(*m*-dioxane). For purposes of abbreviation this compound is referred to as diallylidene pentaerythritol or DAP. In the second stage the DAP reacts with the polyhydroxy compound (shown here as glycerol) in the presence of a curing agent to form a polyether type of polymer. Orth (*5*, *6*) showed that strong acids were the best curing agents.

The present investigation has extended this original work of Schulz, Wagner, and Orth with the resins derived from the unsaturated bisacetals of pentaerythritol. Improvements have been made in the preparation of these acetals, and the mechanism of their polymerization has been studied. The original work has been broadened to include dimethallylidene and dicrotylidene pentaerythritols. Several resins previously unreported have been prepared by a reaction of unsaturated bisacetals in new combinations with polyhydroxy compounds and dibasic acids. The physical properties of these resins have been measured and their applications in castings, laminates, and coatings evaluated.

EXPERIMENTAL PROCEDURE AND DATA

Preparation of Diallylidene Pentaerythritol. Pentaerythritol (139 grams) and acrolein (456 grams) were charged to a 2-liter round-bottomed flask equipped with a nitrogen inlet, thermometer, stirrer, and reflux condenser. Phosphoric acid (85%, 5.9 grams) was added, and the batch was brought up to reflux temperature with stirring and held at reflux temperature for 3 hours. Then fresh acrolein was added continuously through a dropping funnel while the distillate was removed by replacing the reflux condenser with a distilling head. The acrolein addition and distillation were maintained at the same rate in order not to change the batch volume. When a total of 1140 ml. of fresh acrolein had been added, the catalyst was neutralized with 10.3 grams of sodium bicarbonate. The unreacted acrolein was then stripped off under approximately 20-mm. pressure and the batch was diluted with 700 ml. of cold water. The diallylidene pentaerythritol crystallized immediately and was filtered off and dried in vacuum desiccator over potassium hydroxide. The product weighed 194 grams and had a melting point of 42° to 43° C. The DAP was recrystallized from aqueous methanol to give a 92% recovery of purified product. Found: 62.06% carbon, 7.63% hydrogen. Theoretical: 62.25% carbon; 7.60% hydrogen.

Preparation of Dimethallylidene Pentaerythritol. Pentaerythritol (119 grams) and methacrolein (488 grams) were charged to a 2-liter round-bottomed flask equipped with a nitrogen inlet, thermometer, stirrer, and drying tube. A 25-gram phosphoric acid mixture consisting of 18 grams of phosphoric acid (85%) and 7 grams of phosphorus pentoxide, was added to the stirred batch at room temperature. The temperature gradually increased to 39° C. during a 20-minute period as all of the pentaerythritol dissolved. The batch was stirred for a total of 2 hours at temperatures between 25° and 39° C. The unreacted methacrolein was then stripped off under vacuum and the batch was neutralized with 21 grams of sodium hydroxide dissolved in a minimum of water. The dimethallylidene pentaerythritol was filtered off and dried in a forced draft air oven at 90° C. The dried product weighted 178 grams and had a melting point of 115-16° C. Found: 65.2% carbon, 8.42% hydrogen. Theoretical: 65.1% carbon; 8.37% hydrogen.

Preparation of Dicrotylidene Pentaerythritol. Pentaerythritol (122 grams) and crotonaldehyde (500 grams) were charged to a 2-liter round-bottomed flask equipped with a nitrogen inlet, thermometer, stirrer, Dean Stark water trap, and reflux condenser. Phosphoric acid (85%, 5.2 grams) was added and the batch heated to reflux temperature with stirring. The water of acetalization was collected in the trap as formed, and the refluxing crotonaldehyde was recycled to the batch. After 2½ hours of refluxing, 29 ml. of water was collected in the trap and the batch was then neutralized with sodium bicarbonate. The unreacted crotonaldehyde was stripped off under vacuum and the batch was slurried in cold water until crystallization of the product occurred. The product was dried in a vacuum desiccator over potassium hydroxide. This crude dicrotylidene pentaerythritol (205 grams) was purified by vacuum distillation to give a fraction 125° to 130° C. at 0.4 mm. that had a melting point of 43° C.

Reaction of Unsaturated Bisacetals of Pentaerythritol with Polyhydroxy Compounds. Polymerization techniques used were essentially those described in detail by Orth (*5*, *6*). A half mole of the unsaturated bisacetal of pentaerythritol was allowed to react with each hydroxyl equivalent of the polyhydroxy compound. The bisacetal and polyhydroxy compound were fused at 60° to 70° C. with stirring under a nitrogen atmosphere. The curing agent (0.3 to 0.6% by weight) was then added and the temperature was raised to 70° to 80° C. The stirring was continued until all of the polyhydroxy compound had passed into solution. As soon as a homogeneous sirup was obtained the precured resin was cast or used for impregnation, etc., before a further build-up in viscosity took place.

Reaction of DAP with a Glycol. DAP (21.2 grams) and propylene glycol (7.6 grams) were heated to 60° C. with stirring under nitrogen and 0.12 grams of boron trifluoride etherate was added. The batch was heated under nitrogen at 80° C. for 6 hours. An amber colored rubber was formed that was insoluble in dimethyl formamide, acetone, dioxane, chloroform, methanol, and water. The rubber decomposed at 270° C. without melting.

Reaction of DAP with Dicarboxylic Acids. When 21.2 grams of DAP and 11.6 grams of maleic acid were fused together at 80° C. for 1 hour with stirring under nitrogen the maleic acid went into solution. The sirupy resin was then poured into a mold and cured at 90° C. for 16 hours. The cured resin was a soft rubber that was insoluble in styrene at 120° C.

Glutaric acid (13.2 grams) DAP (21.2 grams) and ethanesulfonic acid (0.082 grams) were fused together under nitrogen at 85° C. with stirring. After ½ hour under these conditions the precured sirup was poured into a mold and cured for 22 hours at 90° C. The resin was an amber colored rubber that was insoluble in the common organic solvents.

Curing of the Resins. Various curing agents were tested at concentration levels between 0.3 and 0.6% by weight for their effectiveness in curing the DAP-sorbitol resin. The precured sirup was poured into aluminum foil cups and heated in an oven at temperatures between 85° and 112° C. The curing period was considered to be the minimum time in the oven required to give a hard resin. The results with those curing agents giving satisfactory cures are reported in Table I. Among those agents having no curing action were chlorodifluoroacetic acid, dichlorofluoroacetic acid, oxalic acid dihydrate, phosphoric acid (85%), and triphenylmethyl chloride.

The effect of time and temperature on the curing cycle of the DAP-sorbitol resin with *p*-toluenesulfonic acid as curing agent was measured (Table II).

Table I. Curing Agents for DAP-Sorbitol Resin

Curing Agent	Curing Agent, Wt. %	Curing Period, Hours	Curing Temp., °C.	Color of Resin
p-Toluenesulfonic acid	0.30	0.50	112	Yellow
Boron trifluoride etherate	0.33	6	90	Trace of yellow
Boron trifluoride diacetic acid	0.22	96	90	Light yellow
Boron trifluoride dihydrate	0.30	24	90	Light yellow
m-Benzenedisulfonic acid	0.30	0.33	85	Light orange
Ethanesulfonic acid	0.30	0.50	90	Light yellow
$SnCl_4.6H_2O.HCl$	0.60	1.5	105	Light yellow

Table II. Physical Properties of DAP-Sorbitol Polymer vs. Curing Conditions with *p*-Toluenesulfonic Acid

Temperature, °C.	90				112		
Curing period, hours	4	7.5	12.5	48	0.75	1.5	2.25
Rockwell hardness, M-scale	96	103	104	108	71	81	81
Compressive strength, p.s.i.	35,600	37,100	33,600	29,200	15,600	30,000	28,750
Flexural strength, p.s.i.	18,250	18,650	18,400	20,300	18,300	14,870	17,530
Tensile strength, p.s.i.	6,900	8,635	9,765	11,670	...	...	...

Schulz and Wagner (*10*) showed that the polymerization of these resins could be stopped by addition of amines. The authors found that triethanolamine was the best of several amines tested because it imparted no color to the cured resin. By contrast, ethylenediamine produced a dark brown product. Addition of just enough triethanolamine to neutralize the curing agent stopped the polymerization, but allowed the curing cycle to be started again at its former velocity by adding fresh curing agent to the "stabilized" sirup and curing under the usual conditions. The effectiveness of triethanolamine in stopping the polymerization is shown by the following data for a solution of the stabilized sirup in a solvent mixture of 33% methyl isopropyl ketone, 33% Cellosolve, and 34% xylene.

Days at Room Temperature	Viscosity: Gardner scale (*6*)	Viscosity: Approx. poise
0	C	0.85
2	E-F	1.30
7	E-F	1.30
90	E-F	1.30

A gallon of the nondiluted stabilized DAP-sorbitol sirup was shipped and stored for several months without showing a noticeable increase in viscosity.

Molding of Unfilled Resin Bars for Physical Tests. *p*-Toluenesulfonic acid at 0.30% concentration was used as the curing agent in the investigation of the physical properties of the polymers prepared from polyhydroxy compounds and the unsaturated bisacetals of pentaerythritol. Following the procedure of Orth (*5, 6*), the *p*-toluenesulfonic acid was dissolved in an equal weight of *n*-butyl acetate and this solution was added to the resin melt at 60° C. The mixture was then heated between 70° and 80° C. with stirring under nitrogen until a homogeneous sirup was produced. The sirup was immediately poured into a mold before its viscosity increased. The mold was made from two 13 X 13 inch glass panes held apart on three sides by ⅛-inch silicon rubber gaskets ½-inch wide. The inside dimensions of the mold were 12 X 12 X ⅛ inches. Because the cured resin adhered tenaciously to glass, the panes were covered on the inside with 1-mil Mylar film to which the resin had little adhesion. Screw clamps held the Mylar-coated panes tightly to the rubber gaskets to prevent leakage of resin during curing. The mold was supported in an erect position with the nongasketed end up. The resin was poured slowly into the top of the heated mold in order not to trap air, and the filled mold was placed in a constant temperature oven at 80° C. for 20 hours. The following resins were prepared by this procedure; DAP-sorbitol, DAP-trimethylolpropane, DAP-trimethylolethane, DAP-1,2,4-butanetriol, DAP-glycerol, DAP-1,2,6-hexanetriol, DAP-mannitol, DAP-α-methyl glucoside-glycerol, DAP-water, dicrotylidene pentaerythritol-sorbitol, and dimethallylidene pentaerythritol-sorbitol.

The molded panels of these resins were sawed into suitable bars for ASTM tests (Table III). The values for the epoxy resins are average values for commercial resins (*3*).

Preparation of DAP-Sorbitol Laminates. The DAP-sorbitol resin, because of its excellent physical properties, was selected for testing in laminate formation. Glass cloth (No. 181-114) was dried in an oven for an hour at 110° C. and then dipped for 6 to 7 seconds into the DAP-sorbitol sirup (containing 0.3% *p*-toluenesulfonic acid) at 80° C. As the impregnated glass cloth was withdrawn from the resin bath a scraper blade removed the excess resin. The impregnated cloth was then precured for 15 to 30 minutes in an oven at 80° C. in order to build up the viscosity of the resin before applying pressure. The precured impregnated cloth was then cooled to room temperature and cut into 7 X 7 inch pieces. The pieces were stacked to form a 12-ply thickness so that alternate layers had the longitudinal weave of the cloth in the same direction and neighboring layers had their weave perpendicular. The stack was placed in a Preco press for 1½ hours at 90° C. under gradually increasing pressure. The laminate which was approximately ⅛ inch thick was removed from the press and given a final cure at 90° C. for 16 hours without pressure, but with sufficient bracing to prevent warping. The physical properties of these laminates are given in Table IV.

Preparation of DAP-Sorbitol-Cellulose Combination. DAP was fused with 60% of the stoichiometric quantity of sorbitol and 0.6% ethanesulfonic acid and the resinous sirup used to impregnate cellulose mats. Three cellulose mats (6 X 6 inches) had the resinous sirup applied to their surfaces with a brush. The resin saturated mats were placed in an oven at 90° C. for ½ hour to precure. The three precured mats were then placed on top of one another in the Preco press at 110° C., and pressure was very gradually applied over a period of ½ hour until 80 p.s.i. was obtained. Over a period of 4 hours the pressure was increased to 280 p.s.i. The combination was then removed from

Table III. Physical Properties of Polymers from Unsaturated Bisacetals of Pentaerythritol

Resin	DAP-Sorbitol	DAP-Trimethylolpropane	DAP-Trimethylolethane	DAP-1,2,4-Butanetriol	DAP-Glycerol	DAP-1,2,6-Hexanetriol	DAP-Mannitol	DAP-40% α-Methyl Glucoside-60% Glycerol	DAP-H_2O	DCP-Sorbitol	Epoxy Range
Izod impact, ft./lb. sq. in. notch	0.46	0.49	0.69	1.20	1.07	1.62	0.37	0.44	...	.0.35	0.25–0.45
Rockwell hard.	M-108	M-56	L-90	M-46	M-48	R-65	M-74	R-122, L-46	M-102	M-86	M80–M100
Heat distortion temp., °C.	97	55	65	53	44	37	55	49	80	80	46–293
Compressive strength, p.s.i.	29,200	31,635	26,870	27,380	31,600	27,700	12,300	14,500	...	...	15,000–18,000
Tensile strength, p.s.i.	11,670	9,710	7,610	8,680	5,600	4,690	6,320	3,860	...	...	4000–13,000
Flexural strength, p.s.i.	20,300	15,740	15,280	14,890	13,100	9,770	11,840	13,300	19,900	14,850	14,000–19,900
% elongation of 2 inches	3.15	1.76	2.63	3.60	3.77	12.05	1.88	...	...	...	...
Humidity expansion & contraction											
0-90	+0.08	0	+0.01	+0.04	+0.08	+0.04	+0.01	+0.08	+0.08	+0.10	+0.08
0-90-0	+0.02	-0.01	-0.07	0	-0.03	-0.03	-0.01	+0.03	+0.00	+0.04	0.13
Water absorption, %	1.02	0.43	0.32	0.60	1.6	0.61	0.29	1.18	...	1.24	0.08–0.13

Table IV. Physical Properties of DAP-Sorbitol-181-114 Glass Cloth Laminates

Laminate No.	DAP-S-1	DAP-S-2	DAP-S-3	Epoxy Range
Glass content, %	52	66	68	. . .
Precure time at 90° C., min.	55	30	35	. . .
Laminating pressure, p.s.i.	100	100	140	10–1800
Rockwell hardness	M-114	M-109	M-108	M105-120
Izod impact, ft. lb./sq. in. notch	8. 6	14. 0	11.2	10-25
Compressive strength, p.s.i.	50, 500	55, 500	73, 950	50, 000-90, 000
Flexural strength, p.s.i.	53, 250	58, 500	69, 100	45, 000-80, 000
Tensile strength, p.s.i.	33, 800	. . .	. . .	33, 000-50, 000
Water absorption, %	0. 14	. . .	. . .	0. 05-0. 25
Humidity expansion and contraction				
0-90	+0. 06	. . .	. . .	. . .
0-90-0	+0. 01	. . .	. . .	. . .
Heat distortion temp., °C. (no deflection)	. . .	> 200	> 200	179-191
Elongation of 2 inches, %	1. 70	. . .	. . .	. . .

the press and cured in an oven for 18 hours at 90° C. between two steel plates. The combination contained 34% cellulose and had the following physical properties when compared to the DAP—60% sorbitol resin.

	DAP-Sorbitol-Cellulose Combination	DAP-60% Sorbitol Resin
Flexural strength, p.s.i.	15,920	12,530
Heat distortion temp., °C.	129	47
Rockwell hardness	M-82	M-65

Preparation of DAP-Sorbitol and Epon 1001 Coatings. DAP (212 grams), sorbitol (61 grams) and ethanesulfonic acid (2.2 grams) were stirred together in an open flask at 90° C. The mixture became homogeneous after ½ hour and was cooled to 40° C. and dissolved in a mixed solvent of 33% methyl isobutyl ketone, 33% Cellosolve, and 34% xylene. Sufficient resin was added to the solvent mixture to bring the viscosity between C and F values on the Gardner viscosity scale (*2*).

The epon resin coating was a commercial preparation referred to as an Epon 1001-ethylenediamine coating (*8*). Epon 1001, 97%, and Bettle 227-8, 3% were dissolved in the solvent mixture of 33% methyl isobutyl ketone, 33% Cellosolve, and 34% xylene. To this solution was added an amine solution consisting of 50% ethylenediamine, 17% 1-butanol, 17% toluene, and 16% water (*11*).

Both the DAP-sorbitol and Epon 1001 coating solutions were applied to glass, tin, steel, aluminum, Mylar, polyethylene, and cardboard. The coatings were air-dried 19 hours and then cured 12 hours at 90° C. The comparisons of the physical tests (*2*) on these two coatings are given in Table V.

DISCUSSION

The general equation for the formation of the polyether acetals indicates that if a dihydroxy compound or glycol reacts with DAP a linear polymer would be formed. This hypothesis was tested by allowing DAP to react with propylene glycol; however, the product had all of the physical characteristics of a cross-linked resin. A possible explanation would be that the acetal linkages of DAP open up under the influence of the acid curing agent and react with neighboring polymer chains. It might suggest that this is the main polymerization reaction and that it is unnecessary to have unsaturated groups for polymer formation. To clarify this point infrared absorption studies were run during the curing of a DAP-polyhydroxy resin. The disappearance of the double bonds and hydroxy groups was easily followed on the infrared curves, thereby proving that breaking of the acetal linkages of DAP alone was not the only reaction contributing to polymer formation.

Schulz and Wagner (*10*) prepared DAP in 79% yield from pentaerythritol by running the reaction at the reflux temperature of acrolein for 19 hours in the presence of 0.25% oxalic acid catalyst. Then they neutralized the catalyst with sodium hydroxide and distilled off the unreacted acrolein and the water. A resinous mass was left in the reaction vessel from which the DAP could be vacuum distilled at 107° to 115° C. and 2 mm. of mercury, producing a DAP of high purity in 90% yield in a 4-hour reaction period without the necessity of vacuum distillation of the product. The improved procedure was partly due to selection of the catalyst and to the technique of removing the water of acetalization from the reaction. Phosphoric acid was a sufficiently strong acid to catalyze the acetalization but it did not add to the vinyl group of acrolein or cause the acrolein to polymerize (hydrochloric and sulfuric acid were particularly bad in promoting these side reactions). It was important to remove the water of acetalization from the batch as it was formed because of the reversible nature of the reaction. During the distillation an azeotrope containing 2.6% water and 97.4% acrolein was removed. The water was soluble in the acrolein and could not be separated so that the acrolein could be recycled. It was necessary, therefore, to add dry acrolein to the batch during the distillation. Sodium bicarbonate was used as the catalyst neutralizer at the end of the reaction because it was found that stronger bases caused polymerization of the excess acrolein. After removal of the excess acrolein it was necessary to slurry the reaction mixture with water in order to cause the DAP to crystallize. The water dissolved the sodium phosphate, unreacted pentaerythritol, and monoacetal of pentaerythritol.

The preparation of dimethallylidene pentaerythritol was easier than the preparation of DAP. Methacrolein did not polymerize with itself under the influences of acids and bases like acrolein. Higher acid catalyst concentrations and stronger bases for neutralization were permissible. Methacrolein and water

Table V. Physical Properties of DAP-Sorbitol Coating vs. Epon 1001 Coating

Coating	DAP-Sorbitol	Epon 1001-Ethylenediamine
Flexibility-⅛-inch Mandrel test	Pass	Pass
Sward hardness	56	43
Weatherometer, hours	No attack after 222 hours	No attack after 222 hours
Boiling water resistance, 3 hours	Unaffected	Bleached white
Solvent resistance, 184 hours at room temp.	Attack by ethyl alcohol and methyl ethyl ketone, inert to pet. ether, carbon tetrachloride, and xylene	Attack by ethyl alcohol and methyl ethyl ketone, inert to pet. ether, carbon tetrachloride, and xylene
Acid resistance, 3% HCl, 185 hours	Good	Good
Alkali resistance, 3% NaOH, 185 hours	Poor	Good

formed an azeotrope that separated into a water and a methacrolein layer. Although the azeotropic technique was not used in this preparation, it would have been possible to trap the water of acetalization and recycle the methacrolein layer as in the preparation of dicrotylidene pentaerythritol. This technique probably would have enabled yield of dimethallylidene pentaerythritol to be raised above 85%.

Dicrotylidene pentaerythritol was prepared in 95% yield by the azeotropic distillation technique wherein the water was trapped and the crotonaldehyde recycled. Crotonaldehyde readily formed color bodies and impurities, and even vacuum distillation of the dicrotylidene pentaerythritol failed to give a sufficiently pure product in order to prepare lightly colored resins. The importance of obtaining the unsaturated bisacetals of pentaerythritol in a pure state before polymerization could not be overemphasized if light colored resins of optimum physical properties were desired. Recrystallization from aqueous methanol frequently gave the purification necessary.

Table I shows the relative effectiveness of various curing agents in curing DAP-sorbitol resins. A short curing period and a light colored product were most desirable if these resins were to find commercial use. *m*-Benzenedisulfonic acid gave the fastest cure but a highly colored resin. Boron trifluoride etherate gave a slow cure but the lightest colored resin. *p*-Toluenesulfonic acid and ethanesulfonic acid were considered the best compromise on rate of cure *vs.* color.

In Table II is tabulated a study of the rate of cure *vs.* temperature of cure using *p*-toluenesulfonic acid. A higher mechanical strength and hardness of the resin was achieved after a 4-hour cure at 90° C. than after a 2¼-hour cure at 112° C. The resin also cured at 112° C. had a poorer color than that cured at 90° C. At a curing temperature of 90° C. after 7½ hours little gain in mechanical strength was obtained.

The physical properties of the unfilled resins produced from the unsaturated bisacetals of pentaerythritol with polyhydroxy compounds are tabulated in Table III. The DAP-sorbitol resin had the greatest hardness, highest heat distortion point, and the best tensile and flexural strength. This confirms Orth's (*5*, *6*) finding that the hexahydroxy alcohols form the best resins with DAP. On the other end of the scale the DAP-hexanetriol resin was exceptional for its high Izod impact strength and per cent elongation. This resin also was unusually soft and had a low heat distortion point, tensile strength, and flexural strength. The methylene groups in a polyhydroxy compound like 1,2,6-hexanetriol appeared to have a plasticizing action on the polymer.

The properties of the DAP-trimethylolpropane, DAP-trimethylolethane, DAP-1,2,4-butanetriol, DAP-glycerol, and DAP-mannitol resins were all intermediate between those of the DAP-sorbitol and DAP-1,2,6-hexanetriol resins. It was surprising that mannitol gave a resin of such different properties from its isomer sorbitol, especially since Orth (*6*) found the physical properties of the sorbitol and mannitol resins essentially equivalent. Mannitol seemed to be less compatible with DAP than sorbitol, and possibly unreacted mannitol was present in the cured resin. Similarly, α-methyl glucoside was found incompatible with DAP. In order to overcome this incompatibility, 40% by weight of α-methyl glucoside was mixed with 60% by weight of glycerol, and the resulting mixture allowed to react with DAP. The properties of the resulting resin, however, were inferior to the DAP-glycerol resin.

A most interesting resin was prepared by a DAP and water reaction. In hardness, heat distortion point, and flexural strength this resin was second only to the DAP-sorbitol resin. Furthermore, the DAP-water polymer showed the fastest rate of cure of all the resins. Almost colorless resins could be made from DAP and water by curing at room temperature. Water could also be used as a co-reactant with polyhydroxy compounds, and several DAP-water-sorbitol combinations not reported in this article produced fast curing light colored polymers. The presence of water improved the compatibility of several polyhydroxy compounds that otherwise gave difficult reactions with DAP. Some of the polyhydroxy compounds that gave compatibility problems with DAP so that stiochiometric quantities would not react were inositol, amylose, poly(vinyl alcohol), pentaerythritol, and kojic acid.

Dimethallylidene pentaerythritol was extremely unreactive with sorbitol, and an exceptionally long period was required to give a cure. The resin was so brittle that further polymerization work with dimethallylidene pentaerythritol was considered unpromising. The dicrotylidene pentaerythritol-sorbitol resin was a dark brown, opaque product, but had other good physical properties (Table III). Unfortunately, efforts to incorporate antioxidants and purify the dicrotylidene pentaerythritol did not improve the color significantly.

It is interesting to compare the average values of the physical properties of the commercial epoxy resins (*3*) with the best DAP-polyhydroxy resins in Table III. In general it can be said that the DAP-polyhydroxy resins have physical properties equivalent to the epoxy resins with the exception of lower heat distortion points. Recent electrical data also show that the dielectric constants and power factors of the DAP-polyhydroxy resins are equivalent to those of the epoxy resins. Shorter curing periods are probably necessary to make the DAP-polyhydroxy resins competitive to the epoxy resins. One advantage of the DAP-polyhydroxy resins over the epoxy resins is that they apparently do not cause skin allergies. Traces of acrolein evolved during curing cause eye irritation, however, if adequate ventilation is not used.

The soft amber colored rubbers produced by a reaction of DAP with dicarboxylic acids may have possible applications not yet developed. In the case of maleic acid with DAP in the absence of a curing agent, it may be possible to form an intermediate that may be cross-linked with styrene in the presence of a free radical initiator. This product might have interesting properties when compared to other thermosetting polyester resins.

The properties of the DAP-sorbitol glass cloth laminates reported in Table VI compared favorably with the published values of the epoxy laminates (*3*) shown in column 4. These values are based upon maximum and minimum figures submitted by the manufacturers for unknown glass fabric bases. The properties of the DAP-sorbitol glass cloth laminates improved as higher glass content in the laminates was achieved. The better properties of DAP-S-3 over DAP-S-2 and DAP-S-1 may also be due to the higher laminating pressure used with subsequent improvement in impregnation of the resin in the cloth. The DAP-sorbitol glass cloth laminates have a higher heat distortion point than that reported for the epoxy laminates, which is surprising in view of the lower heat distortion points reported for the unfilled DAP-sorbitol resin in Table III.

The improvement in the physical properties of the DAP-sorbitol resin (containing only 60% of the stoichiometric quantity of sorbitol) when compressed into cellulose sheets gives evidence that chemical combination has been effected. Whether any of the hydroxyl groups on the cellulose polymer chains reacted with the DAP could be confirmed by trying to extract the resin from the cellulose.

The physical properties of the DAP-sorbitol coating *vs.* Epon 1001 coating are given in Table V. On the metallic panels the adhesion of the DAP-sorbitol resin was inferior to that of the Epon but equivalent on the other substrates. In general, the data indicate that the DAP-sorbitol coating is equivalent to the Epon coating except for its poorer alkali resistance. This deficiency may be explained by the presence of an acid curing agent present in the DAP-sorbitol coating. On the plus side, the DAP-sorbitol coating was harder and had better resistance to boiling water than the Epon coating.

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Effect of Composition and Storage on the Properties of Jet Fuels

A. C. NIXON, C. A. COLE, and H. B. MINOR
Shell Development Co., Emeryville, Calif.

Most of the reactions which cause a fuel to fail from a stability standpoint involve oxygen, either dissolved or as oxygenated compounds formed as a result of previous reaction of atmospheric oxygen with fuel constituents. While this usually involves the hydrocarbon constituents of the fuel, very often minor amounts of nitrogen- and sulfur-containing compounds are involved in the degradation reactions. The end result of such reactions is the formation of soluble and insoluble gum which often causes malfunction of equipment.

STORAGE STABILITY

To meet the demands of military logistics the Air Force must maintain large supplies of jet fuel constantly in storage at various locations around the globe. This fuel must be of sufficient stability to be instantly available for use whenever needed. While the fuel can be kept relatively fresh in some areas by rotation of stocks, this expedient may be impractical in others. It is important then to know what factors contribute to instability and to determine whether the specification tests utilized are adequate to ensure sufficient stability. Jet fuels can, broadly speaking, be made from any hydrocarbon constitutents boiling in the range of roughly 150° to 600° F. One of the important restrictions on the composition of the jet fuel produced is the stability of the blend. Figure 1 shows the effect of desert drum storage on the total and insoluble gum content of four fuels prepared from Texas crudes at the same refinery. They all fall approximately in the JP-3 boiling range. The stability of the blends decreases in the order straight-run, catalytically cracked, thermally cracked, with the composite blend (made up of one third of each of the other fuels) behaving like the cracked samples. This type of behavior is typical of the general order of stability of these classes of fuels and is in agreement with the results of Schwartz, Ward, and Smith (*6*) for the stability of diesel fuels. The variations in the point to point slopes for different time intervals is not the result of experimental error. Characteristically, the rate of gum formation either slowed up during the winter months or the amount present actually decreased, probably because of plating out of the gum on the sides and bottom of the container.

The stability of fuels can be considerably improved by various refinery treatments. The fuels referred to above had all received conventional refinery treatments, but no particular effort was made to hold the treatments at a constant level for purposes of comparison. A laboratory study was made for this purpose (Figure 2). The authors' earlier work had shown that the controlling factor in the stability of a jet fuel was generally the stability of the gas oil portion, that is, the fraction boiling above about 400° F. Accordingly, straight-run, catalytically cracked, and thermally cracked gas oils were obtained from a California refinery; each was treated in various ways and then blended with a stable composite gasoline (⅓ straight-run, ⅓ catalytically cracked, and ⅓ thermally cracked) to make a simulated jet fuel. The fuels were then placed in storage at 110° F. in the presence of excess air.

Figure 2 shows the effects of the various laboratory treatments on the total gum formed after 6 months' storage. The

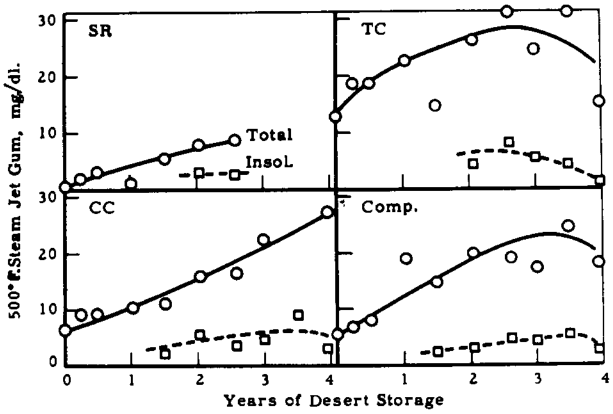

Figure 1. Effect of desert drum storage on the stability of jet fuels from Texas crudes

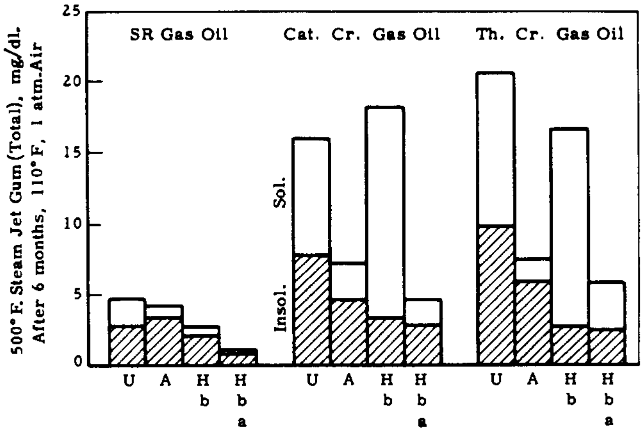

Figure 2. Effect of various treatments on formation of gum in laboratory storage