a large majority of them have been passed as pure. A detailed tabulation of all these results would require too much space, and therefore only a condensed summary of the iodine number (Wijs) and refractive index on approximately one hundred samples, passed as pure during the past few seasons, is included:

	MAXIMUM	Minimum	Average
Iodine number (Wijs)	207.0	193.3	200.4
Refractive index at 25° C.	1.4818	1.4802	1.4811

About 20 per cent of the oils included in the tabulation had indices higher than 1.4815, the limit suggested by Pickard, while none had indices below the lower limit.

During the course of the tabulation, several interesting points were brought to light. The interrelation between the refractive index and iodine number was noted, and the two were plotted against each other. As is shown in the graph, the figures, with very few exceptions, fall within two or three points of a straight line. It will be further noted that the constants on the oils of known purity previously mentioned all fall on or near this line and, moreover, have values approaching both maximum and minimum figures.

Another interesting and extremely significant point is the fact that some of the highest figures were those obtained during recent months, when oil prices were at their lowest, and adulteration "to the analytical limit" was not worthwhile.

From the preceding, the rather contradictory conclusions are that, although in general the oils of highest quality have the highest iodine values and refractive indices, the constants of pure perilla oil (particularly the iodine value and refractive index) are subject to considerable variation, and low values do not necessarily mean adulteration.

#### LITERATURE CITED

 Am. Soc. Testing Materials, 1930 Standard Specification D-125-23.

(2) Pickard, G. H., The Paint Man's Pocket Library, Am. Paint J. Co., Aug. 14, 1922.

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## Phenol-Acrolein Resins

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HE purpose of this work is to investigate McIntosh's reaction for the preparation of the resin "acrolite" (2). The latter is prepared by heating for a long time at 160– 180°C. a mixture of 100 grams of crystalline phenol and 70 grams of glycerol, 1 cc. of concentrated sulfuric acid being used as catalyst. Acrolites obtained in this way are almost black in acid media, purple in basic media, and highly hygroscopic.

The authors made attempts to improve the technical properties of acrolite, first by using another catalyst, and second by varying the proportions of glycerol and phenol. Comparative experiments for the condensation of phenol with glycerol were carried out in the presence of various catalysts, such as sulfuric acid,  $\beta$ -naphthalenesulfuric acid, acid potassium sulfate, and magnesium sulfate. The concentration of each catalyst varied from 0.02 to 0.5 per cent of the total weight of the reaction mixture. The concentration of the reagents varied in the following way: from 1 mole of phenol per 1 mole of glycerol, to 3 moles of phenol per 1 mole of glycerol. The resulting products were, however, darkly colored and highly hygroscopic in all cases.

In the process of the formation of acrolite, two main reactions seem to take place simultaneously: (1) Glycerol is converted into acrolein which then condenses with phenol; (2) glycerol is converted into polyglycerides which condense with phenol. Both suppositions are possible, since, under the influence of sulfuric acid, the formation of acrolein and the formation of polyglycerides take place simultaneously. Therefore, it is possible that acrolite is an intermediate form between phenol-acrolein resins and polyglyceride-phenol resins. Moureu has employed only basic catalysts in the condensation of phenol with acrolein, consequently the authors determined to study the influence of acid reagents on the condensation of phenol with acrolein.

The first experiments with phenol-acrolein resins were carried out by Moureu, together with Dufraisse (4). The authors used basic catalysts exclusively  $(\mathcal{S})$ . Owing to their high elasticity, electrical stability, and the ease with which they can be worked mechanically, these resins were recommended for the molding of all kinds of electrical and radio parts.

Kishi (1) condensed acrolein with phenol under pressure of 30 atmospheres in the presence of salts, such as zinc chloride, aluminum chloride, and other salts which, on being hydrolyzed, might give an acid reaction. Resins prepared by this method possess advantages over phenol-formaldehyde resin, in that they have greater elasticity and viscosity, and that their properties resemble those of synthetic rubber. On being mixed with oils, fats, and natural resins, they yield very viscous mixtures.

From the Japanese patent it is not clear whether the condensation of phenol with acrolein may also be carried out in the presence of acid catalysts under atmospheric pressure and, if so, what the resulting products would be. In this connection, it was decided in these experiments to compare the influence of acid and basic catalysts on the rate of condensation of phenol with acrolein, and to study the kinetics of the condensation process as influenced by time and temperature.

#### PREPARATION OF ACROLEIN

Acrolein was prepared in the following manner:

Five-tenths kilogram of finely powdered anhydrous acid potassium sulfate, 0.1 kg. of finely powdered anhydrous sodium sulfate, and 0.2 kg. of anhydrous glycerol were thoroughly mixed in a 5-liter cylindrical vessel made of copper. The vessel was closed, and the mixture allowed to stand for 24 hours at room temperature.

The reaction vessel contained three openings, one for a dropping funnel used for the addition of glycerol, the second for a mechanical stirrer propelled by an electrical motor, and the third for a condenser. The other end of the condenser was connected by means of an adapter to a large two-necked flask, heated on a water bath to 70-80° C. This flask was connected with another condenser, the second end of which was connected with another flask, through its second neck, was fitted with a reflux condenser, to the upper end of which a calcium chloride tube was attached.

In the first condenser the circulating water was heated to  $40-50^{\circ}$  C.; in the second, colder water (about  $17-20^{\circ}$  C.) was used. The mixture in the copper vessel (after standing for 20 to 24

hours) was heated on an air bath or oil bath to  $195^{\circ}$  C., and that temperature was maintained throughout the whole experiment. The temperature in both condensers and in the middle flask was so regulated that a mixture of condensed water and gaseous acrolein entered the flask, and chiefly gaseous acrolein left the flask. It was found that the best temperature to be maintained in the middle flask was about 70–80° C.



(One mole of phenol per one mole of acrolein; catalysts, same as Table I)

The second two-necked flask (the receiver) contained two layers, the bottom layer consisting of water, saturated with acrolein, and the top layer of acrolein saturated with water. When only a small quantity of glycerol remained in the copper vessel, new portions were added from the dropping funnel so as not to slow up the distillation of acrolein. The quantity of the catalyst mentioned above was ordinarily sufficient for the conversion of 3 kg. of glycerol.

The yield of acrolein was as high as 65 per cent of the theoretical amount based on anhydrous glycerol. The acrolein from the receiver was redistilled by means of an efficient distilling column and was immediately used for condensation experiments.

#### CONDENSATION OF ACROLEIN WITH PHENOL

These experiments were carried on in the following way: a mixture of 10.2 grams of acrolein, 18.8 grams of crystalline phenol (1 mole of acrolein per 1 mole of phenol), and 0.1 gram of acid or basic catalyst was placed in a 100-cc. flask fitted with a stopper carrying a thermometer and reaching under the surface of the mixture. The flask while cooling was rapidly stirred and then placed on a water bath fitted with a stirrer; the temperature of the bath was maintained so as to keep the temperature of the mixture at  $20^{\circ}$  C. throughout the experiment. Every day or two, before the completion of the reaction (i.e., before the mixture was converted into an insoluble condition), the following measurements were made: rate of condensation, viscosity according to Ostwald, melting point according to Kraemer-Sarnow, and flow-point according to Ubbelode.

In order to determine viscosity, the product was dissolved in acetone (nine parts acetone, by weight, per one part resin). Measurements were made at  $20^{\circ}$  C., using an Ostwald viscometer. The results were found from the following relation:

$$n = n_0 \frac{St}{S_0 t_0}$$
  
of acetone

where  $t_0 = \text{time of efflux of acetone}$  $n_0 = \text{viscosity of acetone}$   $S_0 = \text{gravity of acetone}$ 

- t =time of efflux of solution S = gravity of solution
- n = viscosity of mixture

C ....

The following catalysts were tested: acid potassium sulfate,  $\beta$ -naphthalenesulfuric acid, boric acid, potassium hydroxide, barium hydroxide, potassium carbonate, urea, pyridine, and hexamethylenetetramine. It was found that the reaction between acrolein and phenol may be carried out both in the presence of acid and basic catalysts. If the rate of condensation is to be judged by the increase in viscosity of a solution of the condensation product, the following catalysts may be considered most effective: acid potassium sulfate,  $\beta$ -naphthalenesulfuric acid, boric acid, phosphoric acid, and potassium hydroxide. Weak bases, such as barium hydroxide, potassium carbonate, pyridine, hexamethylenetetramine, and urea, influence the rate of the reaction to a much smaller extent (Table I).

TABLE I. EFFECT OF CATALYSTS ON VISCOSITY OF PHENOL Resins

(One mole	of phenol	l per one	mole of	acrolein	)
ALYST	~	V1	SCOSITY	AFTER	DAY

	CATALIEI		- 13	COBLL1 -	ariba L	A18	`
		10	13	16	20	30	38
1.	Acid potassium sulfate	1.360	1.397	1.404	1.458	1.502	1.521
2.	Potassium hydroxide	1.403	1.406	1.413	1.421	1.448	1.470
3.	Hexamethylenetetra-						
	mine	1.360	1.361	1.362	1.378	1.380	1.382
4.	8-Naphthalenesulfuric						
	acid	1.358	1.375	1.388	1.395	1.407	1.413
5.	Barium hydroxide	1.322	1.328	1.336	1.335	1.330	1.338
6.	Boric acid	1.501	1.502	1.504	1.508	1.510	1.512
7.	Potassium carbonate	1.332	1.336	1.342	1.336	1.348	1.361
8.	Urea	1.382	1.427	1.423	1.502	1.507	1.508
9.	Phosphoric acid	1.442	1.464	1.476	1.481	1.473	1.489
10.	Pyridine	1.312	1.334	1.340	1.362	1.365	1.368

From Figure 1, where the abscissa represents time of condensation in days, and the ordinate the viscosity of acetone solution of the resin, it may be seen that the rise of the curves is particularly rapid for such catalysts as acid potassium sulfate, potassium hydroxide,  $\beta$ -naphthalenesulfuric acid, phosphoric acid, and boric acid; and less rapid for urea, barium hydroxide, potassium carbonate, and hexamethylenetetramine.

The other problems to be solved were: (1) to investigate how the rate of condensation, the color of the product, and



(Proportions same as Table II)

its technical properties depended on the mutual proportions of the reagents, if the same catalyst (acid or basic) was used; and (2) to investigate the influence of phenol, cresols, and xylenols on the rate of condensation and the properties of the final products. It was important to solve these questions both from the practical and theoretical points of view, as the solution might lead to the preparation of technically valuable phenol-acrolein resins. In the first series of experiments with

TABLE II. DETERMINATION OF MELTING POINTS OF PHENOL RESINS

	PROPORTION OF PHENO	L					-Melt	ING POIN	T <sup>a</sup> AFTER	DAYS:-					
RESIN	TO ACROLEIN	3	5	8	12	13	15	16	20	23	25	26	28	35	42
	Moles	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
					CATALY	ST, ACID	POTASSIU	4 SULFAT	E						
$15 \\ 14 \\ 25 \\ 26$	1:1 1:1.5 1:3 1:4	32 $44$	27	37.5 46.5	$     \begin{array}{c}       16 \\       38 \\       43 \\       \dots     \end{array} $	58	20  60	24 40 	 	$27 \\ 42.5 \\ 44 \\ 61$	29 44 	45	•••	${}^{34}_{47.5}_{49}_{62}$	• •
$^{13}_{16}$	$1:5 \\ 1.5:1$	51	52	• •	54 	•••	60 	63 	· · · ·	69 22	$\frac{76}{26}$	• •	••	$\frac{82}{32}$	żż
					CATAL	YST, POTA	SSIUM HY	DROXIDE	2						
21	1:2.5	• ·					20		24				<b>27</b>	29	
					CAT	ALYST, P	HOSPHORI	C ACID							
9	1:1					18	18	••	21		24		29	31	38
a Acc	cording to Kraemer-Sarr	now.													

TABLE III. DETERMINATION OF	MELTING	POINTS OF	Phenol Resins
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	PROPORTION OF							T <sup>4</sup> AFTER D	AY8:				
Resin	ACROLEIN	4	8	12	15	17	20	23	24	26	28	30	35
	Moles	° C.	° C.	° C.	° C.	° C.	• <i>C</i> .	° C.	° C.	• C.	° C.	° C.	° C.
					CATALYS	r, ACID POTA	SSIUM SUL	FATE					
15	1:1			30		36	37	38				40	43
14	1:1.5		37	46	2.4	50	• •	59				60	62
25	1:3	40	52.5	53	54	54.5	• •	55.5	• •		• •	••	••
26	1:4	44	60.5	62	65	67	à÷	$\frac{72}{72}$	• •		• •	••	òà
13	1:5		56	60	••	04	67	70	• •	20	••	<b>i</b> ô	41 6
10	1.0:1	• •		• •	••	24	• •	57	• •	29	••	40	41.0
					CATAL	ST, POTASSIU	IM HYDROX	IDE					
21	1:2.5				24	••	29		30	••	31	32	34
4 Acc	ording to Kraeme	r-Sarnov	v.										

an acid catalyst (0.1 part by weight of acid potassium sulfate), the quantitative proportions of the reagents varied in the following order: 1, 1.5, 3, 4, or 5 moles of acrolein per 1 mole of phenol; and 1, 1.5, 2, 3.5, or 5 moles of phenol per 1 mole of acrolein. In the second series of experiments with a basic catalyst (0.1 part by weight of potassium hydroxide), the quantitative proportions of the reagents were the following: 1, 2.5, or 5 moles of acrolein per 1 mole of phenol; and 1, 1.5, or 2 moles of phenol per 1 mole of acrolein.

The mixtures, according to the above-mentioned quantitative proportions, were thoroughly shaken in air-tight flasks that were placed in a cooling bath where the temperature was regulated so as to keep the reaction mixture at  $20^{\circ}$  C. The rate of condensation was measured. The results are given in Tables II-IV.

These experiments show that the rate of condensation in the presence of acid potassium sulfate increases with the increase in the quantity of acrolein, and reaches its maximum when the proportion is 5 moles of acrolein per 1 mole of phenol. In the presence of potassium hydroxide the maximum is reached when the proportion is 2.5 moles of acrolein per 1 mole of phenol. With a further increase of acrolein from 2.5 to 5 moles per 1 mole of phenol, in the presence of potassium hydroxide, the rate of condensation decreases considerably, so that the resinous product even in a month's time is still half liquid with a sharp smell of acrolein. The color of the condensation product is also different, depending upon the mutual proportions of the reagents: products with an acid catalyst and 5 moles of acrolein, and products with a basic catalyst and 2.5 moles of acrolein stand out because of their lighter color; the darkest products were obtained when more than 1 mole of phenol was used per 1 mole of acrolein.

In Figure 2 the ordinates represent the melting temperatures according to Kraemer-Sarnow for products with an acid catalyst, and the abscissas the time of condensation in days. This figure shows that the curves rise rapidly with the increase of the quantity of acrolein per 1 mole of phenol; and, vice versa, with a decrease of acrolein they become more gradual. This same order may be observed in the temperatures of the falling of drops, according to Ubbelode (Figure 3).

The change in viscosity for products prepared in the presence of acid and basic catalysts is shown in Figure 4. The ordinates represent the viscosity of the solution of resins, and the abscissas, the time in days. It may be seen from Figure 4 that at first the curves rise more rapidly for products with an acid catalyst; but later, during the course of condensation, these curves become more gradual and almost parallel to the abscissa axis. The curves for basic catalysts at first rise more slowly, but, when the reaction is nearly ended, their steepness rapidly increases. Such results coincide with those obtained for phenol-formaldehyde resins by Novák and Cech  $(\delta)$ .

It is interesting to note that the maximum rise with an acid catalyst may be observed in the curve for a resin prepared from 5 moles of acrolein per 1 mole of phenol, and with a basic catalyst for a resin prepared from 2.5 moles of acrolein per 1



IGURE 3. DROPPING I EMPERATURES OF PHENOL RESINS (Proportions same as Table III)

mole of phenol. The elementary composition of the resin, prepared by condensing 1 mole of phenol with 5 moles of acrolein in the presence of acid potassium sulfate, varied depending on the purification of the resin. A resin, twice precipitated by water from an acetone solution and dried at  $50^{\circ}$  C. under reduced pressure at 65 mm., showed the following composition: carbon, 56.20 per cent; hydrogen, 6.66 per cent; and oxygen, 37.14 per cent. The same resin precipitated by water from an alcohol solution and dried under the same conditions showed: carbon, 61.47 and 61.80 per cent; hydrogen, 6.32 and 6.32 per cent; and oxygen, 32.21 and 31.88 per cent. The resin residue insoluble in alcohol showed: carbon, 50.96 per cent; hydrogen, 6.96 per cent; and oxygen, 42.11 per cent.

### CONDENSATION OF ACROLEIN WITH HOMOLOGS OF Phenol

English tricresol was divided by distillation in two fractions, boiling at 195-200°, and 200-205° C., respectively. Resins were prepared from them by the same method as was used for phenol.

Thirty-three grams of acrolein (7 moles of acrolein per 1 mole of cresol), 12.96 grams of the cresol fraction, and 0.1 gram of acid potassium sulfate or potassium hydroxide were thoroughly mixed on a water bath. where the temperature was maintained so as to keep the reaction mixture at 20° C. to the end of the reaction, and a little longer for the time necessary to determine the melting point according to Kraemer-Sarnow and Ubbelode, and the viscosity in acetone solution.

The products with an acid catalyst hardened on the second day, but a complete absence of acrolein smell was observed only on the fifth

day. The resins were of a light yellow color.

The products with a basic catalyst (potassium hydroxide) hardened in 1.5 days, but complete absence of acrolein smell was observed after 7 days. The color of the resins was dark yellow.

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DAYS FIGURE 5. DETERMINATION OF MELTING POINTS OF XYLENOL AND CRESOL RESINS WITH ACID CATALYST (Proportions same as Table V)



FIGURE 7. DETERMINATION OF DROPPING POINTS OF XYLENOL AND CRESOL RESINS WITH ACID CATALYST (Proportions same as Table VI)



(Proportions same as Table IV)

The results of the determination of the melting points according to Kraemer-Sarnow for cresol resins are shown in Table V and Figures 5 and 6.

The mixture of xylenols was obtained from the higher fractions (boiling point, 185-250° C.) of purified phenols from coal tar. Purification consisted in treating the fractions with a small quantity of formaldehyde and sulfuric acid in order to get rid of thio-compounds, and then fractionating them between 190-250° C., the distillate being dissolved in a 10 per cent solution of sodium hydroxide and washed with ether and benzene to get rid of hydrocarbons. Free phenols were isolated by passing carbon dioxide through an alkali solution, and were separated, dried with sodium sulfate, and distilled.

The fractions boiling at 200-210° and 210-220° C. were condensed under the conditions previously mentioned. Mixtures of 14.32

grams of the xylenol fraction and 33 grams of acrolein (5 moles of acrolein per I mole of xylenol) with an acid catalyst were converted into a hard resin on the second day, the acrolein smell disappearing on the fifth day. The color of







Р	ROPORTION O	F						- Viecosi		DAVE						
Resin	ACROLEIN	3	7	8	10	12	13	14	18	20	23	27	<b>28</b>	30	33	38
	Moles															
						CATAL	YST, ACH	POTASSI	UM SULFA	TE						
15	1:1			1.362		1.412		1.475			1.547			1,560	1.581	• • •
14	1:1.5			1.382				1.425		1.450	1.477			1.495	1,515	• • •
25	1:3	1.468		1.472		1.482	1.494		1.508		1,528	• • •			• • •	
26	1:4	1.425		1.512		1.582	1.594			1.599	1.608					
13	1:5			1.470				1.515		1.582	1.626		1.635		1.643	
16	1.5:1	· • •		1.341	1,412			1,459			1.566			1.580	1.593	
17	2:1			1.319				1.433		1.462	1.508			1.540	1.566	
18	3.5:1	· • •		1.314	1.352			1.409			1.428			1.440	1.457	
19	5:1			1.302				1.351		1.360	1.364				1.349	
					•	CATA	LYST, PO	TASSIUM	HYDROXII	DE						
20	1:6		1.214			1.234			1.255			1.314				1.420
21	1:2.5		1.161			1.201			1.259			1.316				1.521
22	1:1		1.221			1.242	· • •		1.263			1.319		• • •		1.498
23	1.5:1		1.250			1.281			1.291			1.336	. <b></b>			1.470
24	2:1		1.266			1.296		•••	1.304			1.368				1.452

TABLE IV. DETERMINATION OF VISCOSITIES OF PHENOL RESINS

the products was pale yellow. With a basic catalyst (potassium hydroxide) the product hardened in 1.5 days, and the acrolein smell disappeared after 6 days. The color of the products was pale yellow.

The results of the determination of melting points and viscosities of resins in acetone solution are shown in Tables V-VII, and Figures 5-10.



AND CRESOL RESINS WITH ACID CATALYST (Proportions same as Table VII)

From these figures it may be seen that the maximum rate of condensation belongs to the resin prepared from acrolein and the higher-boiling fraction of xylenol, and the minimum rate to the resin prepared from acrolein and the lower-boiling fraction of tricresol.

#### CHARACTERISTICS OF PRODUCTS

All the resins prepared, before gelatinization in stage A, readily dissolve in acetone, in benzene, and in a mixture of alcohol and benzene; partly dissolve in methyl and ethyl alcohols, and in ether; and difficultly dissolve in turpentine, flax oil, and aliphatic hydrocarbons. Like phenol-formalde-hyde resins, these resins may be converted into an infusible and insoluble condition (stage C) only if the quantity of phenol does not exceed 1 mole per 1 mole of acrolein. The rate of conversion into stage C varies according to the kind of catalyst used and the proportions of phenol and acrolein, as shown in Table VIII.

The rate of polymerization was determined by heating resin

films on glass to  $180-190^{\circ}$  C. in a thermostat, and subsequently dissolving the film in a hot mixture of alcohol and benzene. In case of complete conversion into stage C, the film remained insoluble; in case of partial conversion, there was a partial solution. In this way it was found that the most rapid polymerization was shown by resins prepared from xylenol when the proportion was 5 moles of acrolein per 1 mole of xylenol, and when potassium sulfate was used as a catalyst. Phenol came next with the same catalyst and the same proportion of reagents. Polymerization is much slower for phenol when the proportion is 4 moles of acrolein per 1 mole

TABLE V. DETERMINATION OF MELTING POINTS OF XYLENOL AND CRESOL RESINS

	5 Moles Acrolein per 1		)	1 elti?	NG POIN	T <sup>a</sup> AFTEI	R DAYS:		
Resin	MOLE OF:	1	2	4	7	9	10	11	14
		• C.	° C.	° C.	• C.	° C.	° C.	° C.	° C.
		CATAL	YST, AC	D POT	ASSIUM :	SULFATE			
35	Xylenolb	56		58	62	65	65.5	66	66
36	Xylenol <sup>c</sup>	48		56	57	58	59	59	59
37	Cresold	52		56	56.5	57.5		58	59. <b>5</b>
38	Cresols	54		59	61	64	64.5		65
		CATA	LYST, PO	DTASSI	UM HYD	ROXIDE			
31	Xvlenol a	66.7	67	69	74		75		76
32	Xylenolb	57.5	62	64	67		69		74
33	Cresold	57.5	60	62	65		66		67
34	Cresole	61.5	65.5	66	66.5		68		70
а Ас b 200 d 193	cording to H 0-210° C. 5-200° C.	Kraemer ° 210-2 ° 200-20	-Sarnow 20° C. 05° C.	<i>.</i>					

TABLE VI. DETERMINATION OF DROPPING POINTS OF XYLENOL AND CRESOL RESINS

	5 Moles									
4	ACROLEIN PER	1	— Dr	OPPING	POIN	ITS <sup>a</sup> .	AFTER	R DAYS		
Resin	MOLE OF:	1	2	4	7	8	9	10	11	14
		° C.	° C.	° C.	° C.	° C.	° C.	° C.	°C	. ° C.
	C/	TALYST,	ACID P	OTASSIT	лм вт	LFAT	E			
35	$\mathbf{X}$ vlenol <sup>b</sup>	56		58	62		64		66	69
36	Xvlenol <sup>c</sup>	40		52	56		58		60	62
37	Cresold	52		54	55		57		59	61.5
38	Cresol	54		57	60	••	62		63	64
	с	ATALYST,	POTAS	SIUM B	YDRO	XIDE	£			
31	Xvlenol <sup>c</sup>	69	69.5	72		76			77	78
32	$Xylenol^{b}$	73.5	76	76.5	••	77	••	77.5	••	78
33	Cresold	60.5	67	68	• •	69		70	• •	73
34	Cresole	68	69.5	70		71			71	71.5
a Acc	ording to Ubbe	elode.								
ь 200-	-210° C, c 21	0–220° C								

d 195-200° C. e 200-205° C.

TABLE VII. DETERMINATION OF VISCOSITIES OF XYLENOL AND CRESOL RESINS

	ACROLEIN PER 1 MOLE	r 		V	iscosii	Y AFTE	R DAY	s:		
Resi	N OF:	1	3	5	7	9	10	11	12	14
		CA	TALYST	, ACID	POTAS	SIUM S	ULFATI	3		
35	Xylenol <sup>a</sup>	1.352	1,410		1.466	1.470		· • ·	1.476	1.483
36	Xvlenolb	1.412	1.425		1.444	1.454			1.463	1.471
37	Cresol	1.367	1,403		1.447	1.452			1.456	1.463
38	Cresold	1.375	1.418		1.455	1.462	1.465		. <b></b>	1.471
		(	CATALY	ST, РОЗ	ASSIUM	I HYDR	OXIDE			
31	Xvlenolb	1.523	1.551	1.556	1.594			1.600		1.615
32	Xvlenol <sup>a</sup>	1.481	1.491	1.492	1.513			1,520		1.546
33	Cresol	1.402	1.472	1.480	1,495			1.501		1.527
34	Cresold	1.412	1.505	1.522	1.545			1.551		1.565
a 2 c 1	00–210° C 95–200° C	С. b2 ), d2(	10-220 00-205	°C. C.						

INDUSTRIAL AND ENGINEERING CHEMISTRY



AND CRESOL RESINS WITH BASIC CATALYST (Proportions same as Table VII)

of phenol. When a basic catalyst (potassium hydroxide) is used, and the proportion is 2.5 moles of acrolein per 1 mole of phenol, polymerization goes on still more slowly.

Preliminary experiments showed that phenol-acrolein resins may be used for the preparation of insulating lacquers. The tensile strength and the volume and surface resistance of films

made of these lacquers are quite satisfactory, and, at any rate, are not worse than those made of Bakelite. A great deal depends on the method of preparation of the lacquers and on the solvent and plasticizers used. Table IX shows the results obtained in this laboratory with films of Bakelite, phenolacrolein (resins 13, 25, 26), xylenol-acrolein (resin 31), and cresol-acrolein (resin 34). Cresol- and phenol-Bakelite resins were made using ammonia as catalyst. The data on electrical properties were determined from films (on cigarette paper) after drying at 80° C. (but not polymerization), and after complete polymerization (at 80°C.). Polymerized films were tested immediately after heating and after immersion for 24 hours in water, in ammonia solution (15 per cent), in hydrochloric acid solution (1 per cent), in potassium hydroxide solution (1 per cent), and after remaining in water vapor for 24 hours.

#### SUMMARY

1. The rate of condensation with an acid catalyst reaches its maximum when 5 moles of acrolein per 1 mole of phenol are used, and with a basic catalyst when 2.5 moles of acrolein per 1 mole of phenol are used.

2. With an acid catalyst, the course of condensation is rapid at first, but slows up toward the end of the reaction (stage B); the curves plotted for these rates become almost parallel to the abscissa axis.

3. With a basic catalyst, the rate of condensation is slow at first, but toward the end of the reaction (stage D) the curves for the rates rise rapidly.

4. In the case of cresols and xylenols, the resins have a higher melting point (in stage B) than in the case of phenols.

5. Xylenol-acrolein resins show a higher rate of conversion into an infusible and insoluble condition than other resins.

6. Phenol-, cresol-, and xylenol-acrolein resins may be used for electro-insulating lacquers just as well as Bakelite.

	TABLE VIII.	EFFECT OF CATALYS	r on Conversion of H	Resins into Stage $C$	
Time of Heating at 180-190° C.	5 Moles Acrolein per 1 Mole Phenol in Presence of KHSO4 <sup>a</sup>	4 Moles Acrolein per 1 Mole Phenol in Presence of KHSO46	2.5 Moles Acrolein per 1 Mole Phenol in Presence of KOH <sup>c</sup>	5 Moles Acrolein per 1 Mole Xylenol in Presence of KOH4	5 Moles Acrolein per 1 Mole Xylenol in Presence of KHSO4*
30 sec.	Partial conversion into	No polymerization	No polymerization	No polymerization	Almost complete conversion
60 sec. 120 sec. 180 sec. 6 min. 10 min. 20 min. 40 min.	Complete conversion Complete conversion Complete conversion Complete conversion Complete conversion Complete conversion Complete conversion	No polymerization No polymerization No polymerization No polymerization No polymerization No polymerization No polymerization	No polymerization No polymerization No polymerization No polymerization No polymerization No polymerization Complete conversion	No polymerization No polymerization No polymerization No polymerization No polymerization Complete conversion	Complete conversion Complete conversion Complete conversion Complete conversion Complete conversion Complete conversion Complete conversion
<sup>a</sup> Resin 13. <sup>b</sup> Re	sin 26. c Resin 21. d R	esin 31. e Resin 35.			

TABLE IX.	PROPERTIES	of Resin Films
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		AFTER POLYMERIZATION						
- Resin	After Drying at 80° C.	Immediately after heating	After soaking in 1% HCl soln.	After soaking in 1% NaOH soln.	After soaking in 15% NH <sub>3</sub> soln.	After staying in water vapor	After soaking in water	
	Ohms/cm.2	$Ohms/cm.^2$	$Ohms/cm.^2$	Ohms/cm.2	Ohms/cm.2	$Ohms/cm.^2$	$Ohms/cm.^2$	
SURFACE RESISTANCE								
Xylenol-acrolein Cresol-acrolein Phenol-acrolein Phenol-acrolein Phenol-acrolein Cresol-Bakelite Phenol-Bakelite	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 2.37 \times 10^{10} \\ 2.42 \times 10^{11} \\ 2.23 \times 10^{11} \\ 2.64 \times 10^{11} \\ 1.4 \times 10^{11} \\ 1.01 \times 10^{11} \\ 1.1 \times 10^{11} \end{array}$	$\begin{array}{c} 2.76 \times 10^{10} \\ 1.24 \times 10^{10} \\ 1.09 \times 10^{10} \\ 1.09 \times 10^{10} \\ 4.37 \times 10^{10} \\ \end{array}$	$\begin{array}{c} 1.79 \times 10^{10} \\ 1.54 \times 10^{10} \\ 2.9 \times 10^{10} \\ 1.13 \times 10^{11} \\ 4.4 \times 10^{11} \\ 1.34 \times 10^{10} \\ 8.14 \times 10^{10} \end{array}$	$\begin{array}{c} 7.12 \times 10^{10} \\ 3.86 \times 10^{10} \\ 4.75 \times 10^{10} \\ 1.11 \times 10^{11} \\ 2.58 \times 10^9 \\ 6.54 \times 10^{10} \\ 7.25 \times 10^{10} \end{array}$	$\begin{array}{c} 3.56 \times 10^{10} \\ 1.08 \times 10^{10} \\ 9.06 \times 10^{10} \\ 1.42 \times 10^{10} \\ 1.97 \times 10^{12} \\ 4.38 \times 10^{11} \\ 38 \times 10^{11} \end{array}$	
VOLUME RESISTANCE								
Xylenol-acrolein Cresol-acrolein Phenol-acrolein Phenol-acrolein Phenol-acrolein Cresol-Bakelite Phenol-Bakelite	$\begin{array}{c} 1.22 \times 10^{10} \\ 2.25 \times 10^{11} \\ 1.35 \times 10^{11} \\ 1.06 \times 10^{12} \\ 8.46 \times 10^{12} \\ 1.68 \times 10^{11} \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 1.4 \times 10^{10} \\ 4.55 \times 10^{9} \\ 4.18 \times 10^{9} \\ 1.35 \times 10^{11} \\ 3.96 \times 10^{10} \\ 1.33 \times 10^{11} \\ 3.93 \times 10^{9} \end{array}$	Deterioration Deterioration Deterioration $4.55 \times 10^{9}$ $4.08 \times 10^{9}$	$\begin{array}{c} 1.51\times10^{10}\\ 5.88\times10^{9}\\ 1.28\times10^{10}\\ 4.18\times10^{11}\\ \text{Deterioration}\\ \text{Deterioration}\\ \text{Deterioration} \end{array}$	$\begin{array}{c} 1.83 \times 10^{10} \\ 6.6 \\ 3.46 \times 10^9 \\ 1.83 \times 10^{12} \\ 3.98 \times 10^9 \\ 3.75 \times 10^{10} \\ 6.94 \times 10^9 \end{array}$	$\begin{array}{c} 1.36 \times 10^{12} \\ 6.11 \times 10^{10} \\ 6.23 \times 10^{10} \\ 9.5 \times 10^{11} \\ 9.5 \times 10^{11} \\ 3.5 \times 10^{11} \\ 3.22 \times 10^{10} \end{array}$	
DIELECTRIC STRENGTH <sup>4</sup>								
Xylenol-acrolein Cresol-acrolein Phenol-acrolein Phenol-acrolein Cresol-Bakelite Phenol-Bakelite	$\begin{array}{c} Cm.\\ 36.6\\ 38.2\\ 31.0\\ 47.6\\ 37.2\\ 30.5\\ 31.9 \end{array}$	Cm. 38.1 38.6 32.3 48.1 39.0 37.5 36.1	$\begin{array}{c} Cm.\\ 32.1\\ 36.1\\ 26.1\\ 46.1\\ 35.4\\ 30.2\\ 36.1 \end{array}$	Cm. 30.2 31.0 20.0 40.3 32.0	$\begin{array}{c} Cm. \\ 30.3 \\ 30.8 \\ 21.0 \\ 41.2 \\ 33.1 \end{array}$	$\begin{array}{c} Cm.\\ 31.3\\ 30.2\\ 22.1\\ 40.0\\ 34.1\\ 27.0\\ 26.2 \end{array}$	Cm. 30.3 31.2 22.5 42.3 31.8 30.1 34.2	
	RESIN Xylenol-acrolein Phenol-acrolein Phenol-acrolein Phenol-acrolein Cresol-Bakelite Phenol-Bakelite Xylenol-acrolein Phenol-acrolein Phenol-acrolein Phenol-acrolein Cresol-Bakelite Phenol-acrolein Cresol-acrolein Cresol-acrolein Phenol-acrolein Phenol-acrolein Phenol-acrolein Phenol-acrolein Phenol-acrolein Phenol-acrolein Phenol-Bakelite Phenol-Bakelite	$\begin{array}{c c} -{\rm Resin} & \begin{array}{c} {\rm AFTER \ DRYING} \\ {\rm AT \ 80^{\circ} \ C.} \\ Ohms/cm.^2 \end{array} \\ \hline \\ {\rm Xylenol-acrolein} \\ {\rm Phenol-acrolein} \\ {\rm Cresol-Bakelite} \\ {\rm Phenol-acrolein} \\ {\rm Cresol-Bakelite} \\ {\rm Phenol-acrolein} \\ {\rm Cresol-acrolein} \\ {\rm Cresol-acrolein} \\ {\rm Cresol-acrolein} \\ {\rm Cresol-acrolein} \\ {\rm Stylenol-acrolein} \\ {\rm Stylenol} \\ {\rm Stylenol-acrolein} \\ {\rm Stylenol-acrolein} \\ {\rm Stylenol-acrolein} \\ {\rm Sty$	$\begin{array}{c c} -{\rm Resin} & {\rm Aftrer Drying} \\ {\rm Art 80^{\circ} C.} \\ Ohms/cm.^2 & {\rm Immediately} \\ {\rm after heating} \\ Ohms/cm.^2 & {\rm Ohms/cm.^2} \\ \end{array} \\ \begin{array}{c} {\rm Xylenol-acrolein} \\ {\rm Phenol-acrolein} \\ {\rm Phenol-acrolein} \\ {\rm Cresol-Bakelite} \\ {\rm Phenol-acrolein} \\ {\rm I}.14 \times 10^{12} \\ {\rm S}.2 \times 10^{10} \\ {\rm S}.2 \times 10^{11} \\ {\rm S}.2 \times 10^{11} \\ {\rm S}.2 \times 10^{11} \\ {\rm Cresol-Bakelite} \\ {\rm I}.14 \times 10^{12} \\ {\rm S}.2 \times 10^{11} \\ {\rm Cresol-Bakelite} \\ {\rm I}.9 \times 10^{12} \\ {\rm S}.2 \times 10^{11} \\ {\rm S}.2 \times 10^{11} \\ {\rm Cresol-Bakelite} \\ {\rm Phenol-acrolein} \\ {\rm I}.35 \times 10^{11} \\ {\rm Cresol-Bakelite} \\ {\rm Phenol-acrolein} \\ {\rm I}.68 \times 10^{11} \\ {\rm S}.3 \times 10^{11} \\ {\rm Cresol-Bakelite} \\ {\rm Phenol-Bakelite} \\ {\rm I}.68 \times 10^{11} \\ {\rm S}.7 \times 10^{11} \\ {\rm S}.7 \times 10^{11} \\ {\rm S}.8 \\ {\rm S}.2 \\ {\rm S}.8 \\ {\rm S}.6 \\ {\rm Phenol-acrolein} \\ {\rm S}.2 \\ {\rm S}.6 \\ {\rm S}.1 \\ {\rm Cresol-acrolein} \\ {\rm S}.2 \\ {\rm S}.6 \\ {\rm S}.1 \\ {\rm Cresol-acrolein} \\ {\rm S}.2 \\ {\rm S}.2 \\ {\rm S}.6 \\ {\rm Phenol-acrolein} \\ {\rm S}.2 \\ {\rm S}.6 \\ {\rm Phenol-acrolein} \\ {\rm S}.2 \\ {\rm S}.6 \\ {\rm Phenol-acrolein} \\ {\rm S}.2 \\ {\rm S}.6 \\ {\rm Phenol-acrolein} \\ {\rm S}.6 \\ {\rm S}.1 \\ {\rm Cresol-Bakelite} \\ {\rm S}.6 \\ {\rm S}.1 \\ {\rm Phenol-acrolein} \\ {\rm S}.7 \\ {\rm S}.6 \\ {\rm S}.6 \\ {\rm S}.1 \\ {\rm Phenol-acrolein} \\ {\rm S}.7 \\ {\rm S}.6 \\ {\rm S}.6 \\ {\rm S}.1 \\ {\rm Phenol-acrolein} \\ {\rm S}.7 \\ {\rm S}.6 \\ {\rm S}.6 \\ {\rm S}.1 \\ {\rm S}.6 \\ $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccc} \begin{tabular}{ c ccccc ccccc } \hline After Socking in After so$	

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LITERATURE CITED

(1) Kishi, Niichiro, Japanese Patent 79,157 (1929).

(2) McIntosh, J., IND. ENG. CHEM., 19, 111 (1927).

(3) Moureu, C., and Dufraisse, C., German Patent 382,903 (1920);

French Patent 528,498 (1920); U. S. Patent 1,607,293 (1926).
(4) Moureu, C., and Dufraisse, C., Chem. Zentr., 1924, I, 1715 (B)
(5) Novák, J., and Cech, V., IND. ENG. CHEM., 20, 796 (1928).

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# High-Density Filtration

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In THE old days of the sugar industry the mechanical filtration of sugar liquors was accomplished with various types of gravity filters, such as bag filters, Danek filters, etc. The use of filter aid was unknown, and, as a consequence the rate of flow was rather slow and could be maintained only by carrying proper dilution, usually around 55° Brix, and high temperatures, usually around 190° F. When the various types of pressure filters came into use, filter aids were developed subsequently, which made it possible to obtain a very much increased filtering rate with densities around 60° Brix and with lower temperatures. In the last few years the manufacturers of filter aids have perfected special materials, with the object in mind of increasing still more the rate of flow at higher densities and without sacrificing clarity.

Since it is obviously desirable, from a steam-consumption standpoint, to carry concentrations of dilute products to the highest practical limit, it might be of interest to submit some operating details on a test run made in the refinery of Godchaux Sugars, Inc., in the fall of 1931.

#### DETAILS OF OPERATION

The filtering equipment at that plant consists of the socalled refinery type of Vallez filters, supplied with  $70 \times 80$ monel wire screens. Raw liquors and centrifugal sirups are filtered over the Vallez filter. It had been common practice for years to filter these materials at 176°F. and 60° Brix, using a mixture of slow and fast filter aid.

In explanation, it may serve to state here that the diatomaceous earth used as filter aid in the sugar industry is graded, according to its filtration efficiency, as slow, medium, and fast. Slow and fast filter aids were mixed in order to obtain proper clarity and speed combined. The slow filter aid gives the maximum clarity and minimum filter speed, and the fast filter aid, the minimum clarity with maximum speed. It was common practice to use the slow filter aid for the preliminary coating of the press screens and then follow this with fast pressure filtration, and fast filter aid.

In September, 1931, a test was made covering approximately one month of operating time, during which the fast filter aid was used exclusively. An orifice plate, 1 inch in diameter, was installed in all 4-inch liquor inlet lines to the Vallez filters in order to insure a very gradual pressure increase in the filters during the filtering cycle. This point is essential in obtaining satisfactory results from heavy-density filtration. Beyond that, no mechanical changes were made. Nothing but fast filter aid was used, and the density of the filtrate was increased to  $66.5^{\circ}$  Brix.

Temperatures of the filtrate remained the same (176° F.), and pH was maintained at 7.1 as formerly. Maximum pressure on the Vallez filters at the end of the cycle was 40 pounds, which was slightly in excess of former pressures obtained. Clarity of the filtrate was up to normal standards as measured by a modification of Tyndall's turbidimeter. The following tabulation indicates the advantages obtained:

	NORMAL	HEAVY
VALLEZ FILTERS	DENSITY	DENSITY
Cycles per 24-hour day	38	11
Average filtering time per cycle	2 hr., 46 min.	8 hr., 55 min.
Raw sugar per cycle, tons	27,	85
Filter aid per ton melt, pounds	8.27	6.21
Corrected Brix of filtrate	60	66.5

Since the resulting mud cake sluiced from the Vallez filters is being refiltered over a set of secondary filter presses, designated as mud presses, a brief tabulation shows results obtained there:

	NORMAL	HEAVY
MUD PRESSES	Density	Density
Press cycles per day	15.2	11
Average filtering time per cycle, hours	3.86	6.62
Press mud per ton melt, pounds	20.67	11.87
Sucrose loss per ton melt, pound	0.14	0.10

Here again the advantage of heavy-density filtration shows up clearly in an extension of press cycles, with resulting reduction in sugar losses and production of light sweet water.

Following the changes produced through subsequent char filtration, it was noted that, owing to the heavier concentration carried, it was possible to handle the same volumes of melt over one less char filter, making this char filter available for other purposes. Ash and color removal in char showed an increase with heavy-density filtration, as might be expected because of higher concentration of nonsugars. An increase was noted in the time required to sweeten off the char filters, owing to heavy-density filtration, resulting in an excess production of concentrated sweet water per ton melt. This was particularly noticeable in the fine grist char.

#### SUMMARY

1. Raw liquor can be safely filtered, using high speed filter aid exclusively, at 66-67° Brix density without a sacrifice of clarity.

2. Advantages of high-density filtration are:

a. Economies resulting from reduction in fuel used, reduction in filter aid used, reduction in sucrose losses, and reduced maintenance of filter equipment.

b. Increased capacities of mechanical filtration, char filtration, and subsequent evaporation processes.

3. The disadvantage of high-density filtration is the increased sweet water production in the char house, but this is not sufficient to offset the advantages obtained.

#### ACKNOWLEDGMENT

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