EXPERIMENTAL PLASTICS
AND
SYNTHETIC RESINS

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BY

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PREFACE

Experimental Plastics and Synthetic Resins extends the purpose of *A Laboratory Manual of Plastics and Synthetic Resins*, published in 1943 and intended to supply the members of college and university staffs with techniques and processes which could be used as part of a laboratory course in plastics. Prior to 1943, it was practically impossible for our educators to obtain such necessary information from industry. Since many of the highly successful war applications of plastics were the result of joint efforts by industry and education, it is fitting that industry and education work hand in hand to promote plastics as a branch of science rather than an "industry of recipes." With this thought in mind, the experiments in this book have been revised where necessary to include more detail. In some cases, alternate methods of preparation have been included. The preparation of certain monomers which could not be obtained in small quantities, even though manufactured on a large scale, have been included so that experiments requiring these materials can be performed. The suggested experiments for those desiring to continue their studies in this field have been broadened in scope, not only to extend the principle of the experiment but also to indicate the possible trend of industrial development.

This book, as was the earlier book, is not intended to be a manual of instruction on manufacturing procedures. Rather it aims to demonstrate the chemical reactions used in the preparation of plastic materials. It is intended that the student, by performing these experiments, should abstract certain chemical principles responsible for polymer formation. With this object in mind, the book was planned to eliminate the "spoon feeding" of students and is not meant for those with only a passing interest in plastics. The course is intended for those who have had college organic chemistry or its equivalent. The choice of the experiments is left to the judgment of the instructor since they were not calculated to fill any particular number of laboratory hours. Practically all the well-known resins and plastics which can be prepared readily, even in a small laboratory, have been included.

The prime purpose of each particular experiment is to demonstrate a principle. However, many of the results obtained can be used directly in industrial production; with sufficient study others can be developed to industrial use.

To the many industrial concerns which have found the earlier book of some value in their laboratories the suggestion is made that they consult their legal departments before industrializing their products because the subject matter of some of the experiments of this book falls within the scope of active United States Patents.

The Pro-phy-lac-tic Brush Company graciously sponsored this revision by granting use of the facilities of its Prolon Laboratory and of its organization. For this assistance, the author is very grateful. Generally, it indicates the attitude of industry toward education. The men in education have also been most helpful.

The author expresses appreciation for having read the manuscript and for their kind suggestions to Dr. W. H. Rauscher of Rensselaer Polytechnic Institute and to Dr. P. H. Emmett of Mellon Institute of Industrial Research.

G. F. D'ALELIO

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TEST METHODS

EXPERIMENT 1

PHENOL FOR RESIN PREPARATIONS

Phenol undergoes chemical changes in contact with oxygen and light, with the consequent development from a pink to a dark brown color. For use in laboratory preparations, the phenol should be a colorless crystalline solid, which is obtained by the distillation of phenol at atmospheric pressure (b.p. 183° C at 760 mm). For the following experiments prepare approximately 1000 grams of phenol by distilling about 1400 grams of stockroom phenol from a 2-liter distilling flask. Stopper the distilled phenol well and store out of direct light. When a large quantity of phenol is needed, the phenol can be melted (m.p. 42–43° C) on a steam bath or in a hot-water bath, and the correct amount of liquid phenol can be weighed into a reaction flask.

> *Caution!* Phenol is very *corrosive* and *toxic.* It should never be allowed to come in contact with the skin or hands. If, accidentally, phenol does come in contact with the skin, rinse immediately with water, then with a 95% alcohol solution containing 0.3% ferric chloride. Follow this by continued rinsing with large quantities of water. In all accidents with phenol, consult your instructor as soon as possible. *Use safety goggles or face shields when pouring liquid phenol and wear rubber gloves as a precaution against chemical burns.*

The addition of 6 parts of water to 94 parts of distilled phenol will liquefy the phenol, saving time and eliminating the danger of repeated meltings. In future use, the presence of the water must be taken into account so that, when one mole of phenol is required, 100 grams of phenol-water mixture should be used. If the melted anhydrous phenol is employed, the correction need not be made.

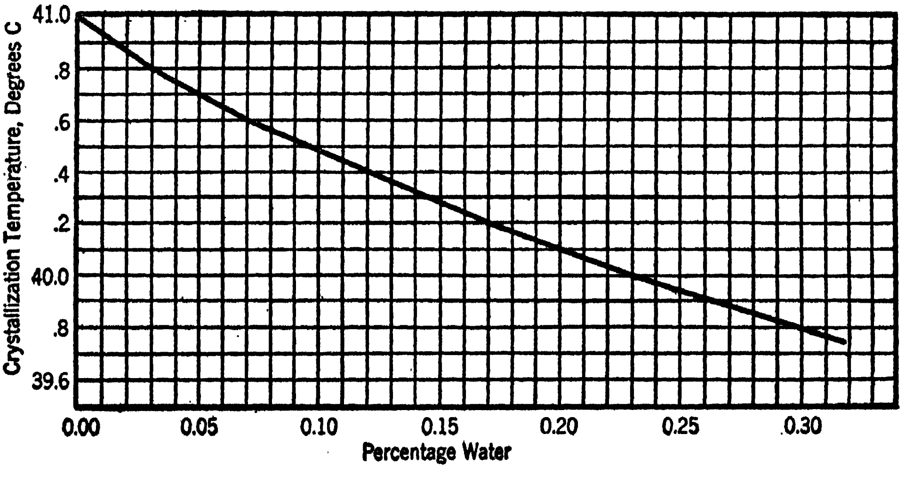


FIGURE 1. Phenol-Water Mixtures.

Prepare six clean screw-cap vials, with aluminum foil as the sealing disk, and treat as indicated below, using water-white distilled phenol.

Vial 1—Fill with phenol, seal, and leave exposed to light.
Vial 2—Half fill with phenol, seal, and leave exposed to light.

Vial 3—Fill with phenol and add a small piece of iron. Seal and leave exposed to light.

Vial 4—Half fill with phenol, seal, and place in a dark place.

Vial 5—Fill with phenol, seal, and place in a dark place.

Vial 6—Fill with phenol. Add one drop of 10% sodium hydroxide solution, seal, and leave exposed to light.

Observe the vials at frequent intervals and note the time required for the phenol to acquire a pink color and to become darkened.

QUESTIONS

1. What is the natural source of phenol?
2. Write and name the phenolic homologues, e.g., all the cresols and xylenols. Give their literature melting and boiling points.
3. Describe the four main industrial processes for the preparation of phenol and write the balanced equations for them. In the preparation of phenol from benzene and air by the direct oxidation process, what by-products are to be expected?
4. Name some of the factors that are responsible for the discoloring of phenol.
5. What color does a ferric chloride solution develop in the presence of phenol?

Suggested Extension

1. Determine the crystallizing point of pure redistilled phenol containing relatively small and large amounts of water. Check the values for the samples containing small amounts of water against Figure 1.

EXPERIMENT 2

FORMALDEHYDE DETERMINATIONS

Formalin, an aqueous solution of formaldehyde, is widely used when anhydrous reaction conditions are not required. The formalin of industry, known as 40% formalin, refers to the percentage volume of gaseous formaldehyde contained in the aqueous solution. It contains approximately 37% by weight of CH_2O; and approximately 80.85 grams of formalin equals one mole of formaldehyde.

Part A

Determine the formaldehyde content of a formalin solution, using the hydroxylamine hydrochloride method (Test Method 1) and the sodium sulfite method (Test Method 2). Compare the values obtained. Since neither method is completely satisfactory for all tests, proficiency should be acquired in both methods.

Part B

Suspend 1 gram of paraformaldehyde in 100 cc of distilled water and allow the mixture to stand for 10 minutes. Determine the formaldehyde content of the solution, and, if the value is not correct, explain why.

Part C

Add 1 gram of trioxane to 100 cc of distilled water and determine the formaldehyde content of the solution. Explain why the test does not accurately indicate the presence of formaldehyde in trioxane and compare the results with those obtained under Part *B*, where paraform is used. If the trioxane solution is first refluxed with a trace of acid, would a formaldehyde test be obtained? Verify your prediction.

QUESTIONS

1. Describe briefly the industrial method of synthesizing formaldehyde from: (*a*) methanol, (*b*) methane. What by-products would be expected in each?
2. Why does industrial formalin contain about 9% methanol?
3. What are the differences between paraformaldehyde and trioxane?
4. In what forms other than the dissolved gas does formaldehyde exist in a formalin solution?
5. Write the formula for polymethylene oxide.

EXPERIMENT 3

PREPARATION AND PROPERTIES OF *o*- AND *p*-HYDROXYBENZYL ALCOHOLS

Preparation of *o*- and *p*-Hydroxybenzyl Alcohols

Dissolve 98 grams of phenol in 480 cc of aqueous 10% sodium hydroxide in a 1-liter flask. To this solution add 30 grams of formaldehyde, using the required volume of formalin, about 80.85 grams. Allow this mixture to stand for at least 24 hours or until the concentration of formaldehyde remains constant. Make the solution neutral to litmus, using approximately 140–145 cc of 50% aqueous acetic acid. Extract the solution three times with ethyl ether, using 50-cc portions. The ether extractions remove the phenol alcohols and uncombined phenol. The ether is removed by distillation in a steam bath. Steam-distill the residue until a sample of the distillate no longer gives a test, i.e., a red color, for phenol with a 3% ferric chloride solution. Extract the residue from the steam distillation three times with ether, using 45–50-cc portions. Dry the ether extract over anhydrous sodium sulfate, filter, and distill the dry ether extract to remove the ether. A yellowish oil is obtained in the distilling flask. Transfer the oil to an Erlenmeyer flask and allow to crystallize in the refrigerator. These crystals are a mixture of *o*- and *p*-hydroxybenzyl alcohol. Divide the crystals into two portions. Save one portion for Experiment 4, and carry out the following experiment with the other.

Separation of *o*- and *p*-Hydroxybenzyl Alcohol

Extract the crystalline mass with benzene at 50° C. The *o*-hydroxybenzyl alcohol is crystallized by concentrating and cooling the benzene solution. The remaining *p*-hydroxybenzyl alcohol is recrystallized from petroleum ether. Determine the melting point of the two fractions.

		Melting Points	
	Yield	*Literature*	*Found*
o-Hydroxybenzyl alcohol	....	....	....
p-Hydroxybenzyl alcohol	....	....	....

QUESTIONS

1. Write the equation for the intermediate reaction products of 1 mole of formaldehyde and 1 mole of phenol. Why are they called alcohols?
2. What is saligenin?
3. Write the reactions for the intermediate alkaline condensation product of 1 mole of phenol with 2 and with 3 moles of formaldehyde.

EXPERIMENT 4

RESINIFICATION OF THE HYDROXYBENZYL ALCOHOLS

Place the following amounts of the substances listed below either in flat-bottomed metal dishes or milk cups and heat the samples for 10 minutes at 140° C on a hot plate or in an oven. Small test tubes immersed in a suitable oil bath may be used if metal cups are not available. For these tests, use the crude mixture of hydroxybenzyl alcohols of Experiment 3.

Note the speed of resinification, if any, and whether the sample is melted, rubbery, or hard at 140° C. After 10 minutes of heating, cool the samples to room temperature and determine their solubility in boiling 10% aqueous sodium hydroxide. If solution occurs, allow the solution to cool to room temperature, make neutral to litmus with 5% hydrochloric acid solution, and note if precipitation occurs. Test another small sample of the heat-treated resins for solubility in ethyl alcohol.

Sample	*Speed of Resinification*	*Condition at 140° C*	*Solubility in NaOH*	*Precipitability*	*Solubility in Alcohol*
A. 1 gram of hydroxybenzyl alcohol	....	....	....	....	....
B. 1 gram of hydroxybenzyl alcohol plus 0.1 gram of phenol	....	....	....	....	....
C. 1 gram of hydroxybenzyl alcohol plus 1 drop of concentrated ammonium hydroxide	....	....	....	....	....
D. 1 gram of hydroxybenzyl alcohol plus 1 drop of concentrated hydrochloric acid	....	....	....	....	....
E. 1 gram of hydroxybenzyl alcohol plus 1 drop of 10% sodium hydroxide solution	....	....	....	....	....

QUESTIONS

1. Write the equation for the resinification of *p*-hydroxybenzyl alcohol. Is it accelerated by alkalies and acids?
2. Does ammonia react with the hydroxybenzyl alcohols? Write the reactions for 1 mole of ammonia with 1, 2, and 3 moles of hydroxybenzyl alcohol and name the products.
3. What was the function of the phenol in Sample *B*?
4. Write the reaction for 1 mole of hydroxybenzyl alcohol and 1 mole of phenol and name the product. What is the mole ratio of phenol to formaldehyde in this compound?
5. Show by writing the reactions that, by increasing the mole ratio of hydroxybenzyl alcohol to phenol, e.g., 2, 3, 4, . . . 10, etc., to 1, the ratio of phenol to formaldehyde approaches 1 and theoretically the reaction can produce a linear molecule of indefinite size.

EXPERIMENT 5

PREPARATION AND RESINIFICATION OF A DIPHENYLOL ALKANE

Preparation of 1,1-Bis(*p*-Hydroxyphenyl)-Ethane

Completely dissolve 11 grams of acetaldehyde (b.p. 21–23° C) in 85 grams of redistilled phenol in a stoppered flask, and cool the solution to 5° C before adding 0.5 cc of concentrated hydrochloric acid. The liquid acetaldehyde may be either purchased or prepared by depolymerizing paraldehyde in the presence of dilute sulfuric acid. Let the mixture stand at room temperature for 24–48 hours and then place the sample in a refrigerator until crystallization appears to be completed. Use a Büchner funnel to filter off the crystals by suction and wash them with 25 cc of cold benzene. Transfer the crystals to a flask and steam-distill until all the unconverted phenol is removed, using a 3% aqueous ferric chloride solution to determine the presence of phenol in the distillate. The resulting product in the flask is allowed to crystallize and is separated from the water by filtration. Dry the resulting crystals overnight in a 50° C oven and then recrystallize them from a mixture of equal parts of benzene and petroleum ether.

Yield		*Melting Point*	
Grams	%	Found	Literature ....

The propane derivative, 2,2-bis(*p*-hydroxylphenyl)-propane, has become industrially available and important. It indicates the type of intermediates obtained in the acid reaction of a phenol and a ketone. To save preparation time, this compound may be purchased as Bis-phenol-A, and used in the remaining part of the experiment.

Resinification of a Bis(*p*-Hydroxyphenyl)-Alkane

Place the following amounts of the stated substances in a flat-bottomed metal dish or milk cup and heat for 10 minutes at 140° C. The substances may be either ethane or propane bisphenol. Small test tubes immersed in an oil bath may be used if metal cups or dishes are not available. Note the speed of resinification, if any, the color of the resin, and whether the sample is melted, rubbery, or hard at 140° C. After 10 minutes, cool the sample to room temperature and test the solubility of a small part of the heat-treated sample in ethyl alcohol and acetone. Record the data in the following table:

Sample	*Color Resin*	*Condition of Resin at 140° C*	*Solubility*	
			Alcohol	*Acetone*
A. 1 gram of diphenylol alkane	....	....	....	....
B. 1 gram of diphenylol alkane plus 0.1 gram of paraformaldehyde	....	....	....	....
C. 1 gram of diphenylol alkane plus 0.1 gram of hexamethylenetetramine	....	....	....	....
D. 1 gram of diphenylol alkane plus 0.1 gram of hexamethylenetetramine plus 0.01 gram of lime	....	....	....	....

QUESTIONS

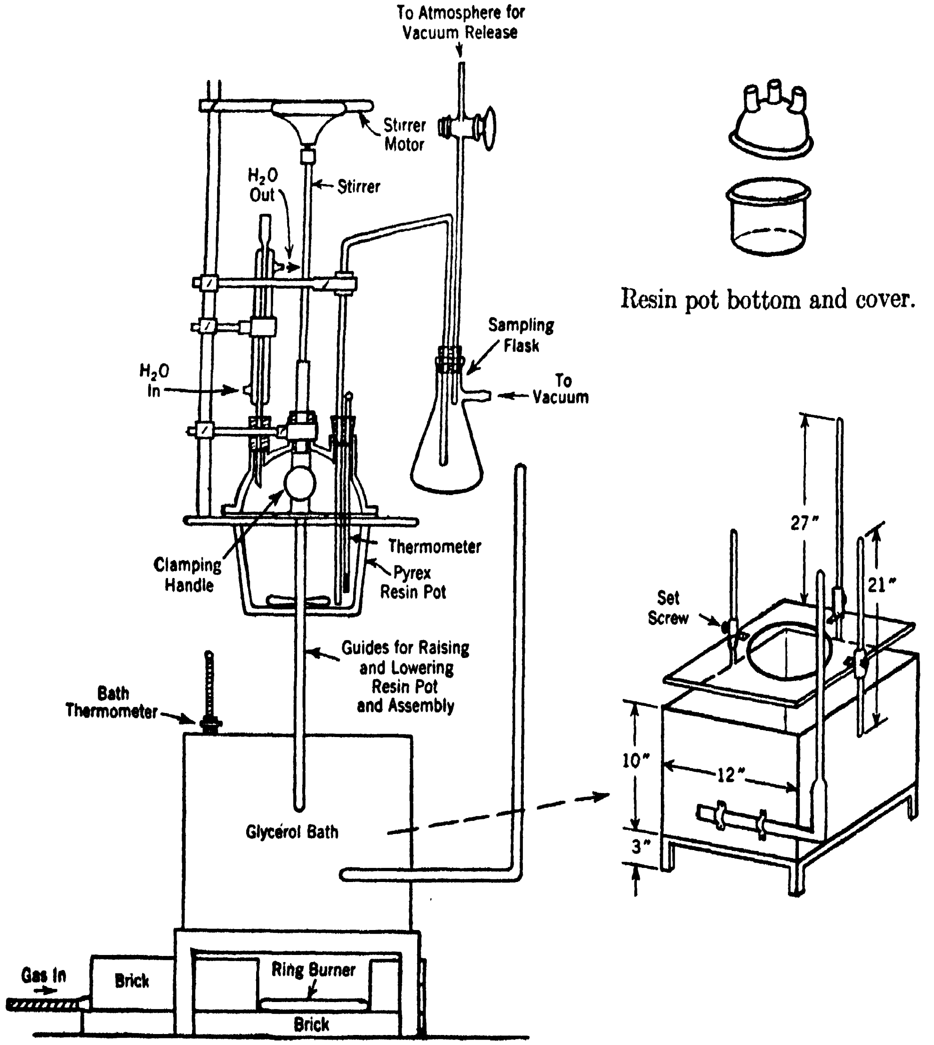
1. Write the acid reactions of (*a*) 1 mole of formaldehyde with 2 moles of phenol, (*b*) 1 mole of acetaldehyde with 2 moles of phenol, and (*c*) 1 mole of acetone with 2 moles of phenol.
2. Contrast the reactions of the acids mentioned in question 1 with the alkaline-catalyzed reactions.
3. What by-products could be expected in the alkaline condensation of acetone with phenol?
4. Does the diphenylol alkane resinify by itself on heating? Explain your answer.
5. What is the effect of (*a*) paraformaldehyde, (*b*) hexamethylenetetramine, and (*c*) the lime?

EXPERIMENT 6

COMPARISON OF ALKALINE CATALYSTS ON THE PHENOL-FORMALDEHYDE RESINIFICATION

Procedure with Sodium Hydroxide as a Catalyst

In a three-necked flask which is arranged (Figure 2) so that it can be heated in a suitable bath and is fitted with a reflux condenser, stirrer, thermometer, and vacuum sampling device place 188 grams (2 moles) of redistilled phenol and 242.5 grams of 37.2% formalin (3 moles of formaldehyde). Start the stirrer, record the temperature of the mixture, and remove a 10-cc sample (00). All samples are to be removed by means of the vacuum sampling device. To the mixed reactants add 1.6 grams of sodium hydroxide previously



Resin pot bottom and cover.

FIGURE 2. Complete Assembly with Resin Pot Removed from Bath. On the Right: Details of Heating Bath Chamber.

dissolved in 20 cc of distilled water and note the time of addition of the catalyst. Note the temperature of the mixture and remove a 30- to 35-cc sample (0). Record the temperature of the bath, which should be maintained throughout the experiment at 125 ± 3° C. Immerse the reaction flask and contents in the heating bath, and note the time of this immersion. Record the time of reflux, when the first drop falls from the condenser, as well as the temperature of the bath at reflux and the temperature of the reaction mixture at reflux. Take 30- to 35-cc samples by means of the vacuum sampler at the intervals indicated in the data sheet, and at the time of sampling read and record the temperature of both the bath and the reaction mixture.

Data and Determinations on Samples

Titrate each of the above samples for formaldehyde content (Test Method 1). Determine the resin content on the 0 and 40-minute samples at least (Test Method 3) and the stroke cure on the last sample taken (Test Method 4). If time permits, obtain sufficient data to supply all the data in the following form:

Data	*Time*
Reactants mixed (sample 00)	....
Catalyst added (sample 0)	....
Immersion	....
Reflux	....

Minutes After Reflux	*Sample*	*Bath Temperature*	*Reaction Mixture Temperature*	*Residual Formaldehyde* (cc of 0.33 *N* NaOH)	*Resin Content*	*Stroke Cure*	*Precipitability*
	00	....	....	....	....	....	....
	0	....	....	....	....	....	....
2	1	....	....	....	....	....	....
10	2	....	....	....	....	....	....
20	3	....	....	....	....	....	....
40	4	....	....	....	....	....	....
60	5	....	....	....	....	....	....
80	6	....	....	....	....	....	....

Ammonia as a Catalyst

Repeat the preceding experiment, using the same amount of phenol (188 grams) and formalin (242.5 grams) and, as a catalyst, 0.04 mole of ammonia (approximately 2.5 grams of concentrated ammonium hydroxide). It is suggested that a microburette be used to measure the ammonium hydroxide. Since ammonia reacts immediately with formaldehyde, the catalyst may be 1.4 grams of hexamethylenetetramine instead of ammonia.

EXPERIMENT 7

PREPARATION OF A PHENOL-FORMALDEHYDE CASTING RESIN

The quality of the casting resin is dependent upon the purity of the ingredients used in its preparation, and upon maintaining these ingredients and their reaction products entirely free of contamination. Some color is formed by cork or rubber stoppers that have to be used in the experiment if ground-glass equipment is not available.

In a thoroughly cleaned three-necked reaction flask, which can be heated to 105 to 110° C by means of a suitable oil or glycerol bath, and fitted with a thermometer, reflux condenser, stirrer, and a vacuum sampling device, place 94 grams (1 mole) of water-white redistilled phenol and 200 grams of approximately 37.2% formalin (2.5 moles of formaldehyde). Dissolve 1.5 grams of potassium hydroxide in 15 cc of water and add this to the phenol-aldehyde solution as the condensation catalyst. Sample the mixture and test for formaldehyde content in grams per 100 cc of solution. Reflux the mixture for 1½ hours, obtaining samples for formaldehyde content at the end of 60, 70, 80, and 90 minutes. Divide the reaction mixture into two equal parts, labeled sample *A* and sample *B*. Consult Experiment 8 before proceeding with the remainder of this experiment.

Treatment of Sample A

Adjust the *p*H of sample *A* to about 6.0, using a 10 to 20% aqueous lactic acid solution. If the solution is cloudy or otherwise contaminated, filter through a double thickness of filter paper. If the solution is too viscous or shows two distinct phases, add 50 cc of alcohol to assist the filtration. Otherwise, dehydrate the solution directly at a pressure of 15 mm and at a bath temperature of 110° C until the temperature of the resin as indicated by a thermometer in the mass of the resin registers 70° C. Break the vacuum and pour a portion of the resin into a clean test tube. Label this sample *A*1. To the remainder of the resin in the flask add 7 to 8 cc of pure glycerol and stir thoroughly. Continue the dehydration at 15 mm until the temperature of the resin reaches 85° C. Pour another casting and label it *A*2. Another casting may be colored by dyeing the resin with a small quantity of glycerol-soluble dye previously thoroughly mixed with glycerol. Label this sample *A*3. Save the samples for Experiment 8.

Treatment of Sample B

Adjust the *p*H of sample *B* to about 6.0 with aqueous citric acid and treat thereafter as in sample *A*. Label the samples *B*1, *B*2, and *B*3, and save for Experiment 8.

QUESTIONS

1. Why is the *p*H adjusted to the acid side before dehydration?
2. Why is the high ratio of formaldehyde used?

Suggested Extensions

1. Keeping the amount of phenol and alkali catalyst constant, investigate a series of reactions wherein the amount of formaldehyde is varied from 1 to 3 moles per mole of phenol in one-quarter mole steps.

2. While maintaining the phenol, formaldehyde, and alkaline catalyst constant, adjust the *p*H of the resin solution to a series of *p*H values prior to dehydration, preferably on the acid side.
3. While maintaining the phenol and aldehyde constant, and using a single alkaline catalyst, investigate the effect of the initial concentration of the alkali. Adjust the *p*H to the same value in all cases before dehydration.
4. Investigate the effects of substituting part or all of the phenol with cresols, xylenols, or other substituted phenols.
5. Investigate the effects of substituting part of the phenol by other materials that condense with formaldehyde, e.g., urea, melamine, dicyandiamide, and acetone.
6. Investigate the use of inorganic acids such as HCl, H_3PO_4, H_3BO_3, etc., as well as other organic acids in the neutralization and acidification of the alkaline condensation product.
7. Study the effect of time and the temperature of the initial condensation upon the color of the dehydrated resins and the cast pieces prepared from them.

EXPERIMENT 8

PREPARATION OF PHENOLIC RESIN CASTINGS

Casting is a process which comprises pouring a potentially heat-convertible liquid resin or monomer into a mold and then hardening it by heat to obtain the desired form through condensation or polymerization. Commercially, lead alloy molds are used for phenolic resin castings and are made by dipping a steel arbor into molten lead. For experimental work, however, ordinary test tubes are satisfactory as removal from the mold consists in merely breaking the tube from the casting. The samples of casting resins of Experiment 7 should about fill a test tube one-half inch in diameter which has been thoroughly cleaned and dried, since dirt may initiate bubbles during the casting process. Since these casting resins are rather viscous liquids, they should be poured while warm, i.e., at about 60 to 70° C. Cure is then accomplished by heating the samples in an oven at 80 to 85° C, for a time to be determined by inspection. Normally maximum properties should be developed in 5 to 8 days unless accelerators are used. Determine the water absorption on all the cured samples and the relative ease with which the sample may be bent after immersion in boiling water for 15 minutes.

Record the data in the following table:

Sample	*Cure Temperature*	*Time Initial Set*	*Time Final Set*	*Transparency*	*Water Absorption*	*Boiling-Water Resistance*
*A*1 Lactic acid	....	....	....	....	....	....
*A*2 Lactic acid plus glycerol	....	....	....	....	....	....
*A*3 Lactic acid plus dye plus glycerol	....	....	....	....	....	....
*B*1 Citric acid	....	....	....	....	....	....
*B*2 Citric acid plus glycerol	....	....	....	....	....	....
*B*3 Citric acid plus dye plus glycerol	....	....	....	....	....	....

With a knife, try whittling pieces of the cast resins, noting which are brittle and which could be easily machined.

QUESTIONS

1. Describe: *a.* The differences between the samples containing citric acid and lactic acid when both are dehydrated to 60° C. *b.* The differences between the samples containing glycerol and those not containing glycerol, when both are dehydrated to 85° C.
2. To what is the opacity of some of the samples due?
3. How would you prepare mottled samples?
4. Does glycerol also act as a plasticizer and softening agent?

Suggested Extensions

1. Consult the A.S.T.M. Standards and determine all physical properties, e.g.:
    1. Flexural strength
    2. Impact strength
    3. Heat resistance
    4. Compressive strength
    5. Specific gravity
    6. Tensile strength, etc.

   as a function of cure time, composition, etc.
2. Study the addition of curing accelerators of the co-reactive type, such as resorcinol and 1,3,5-xylenol. These accelerators are added after the dehydration and just prior to the casting. Plot the cure time as measured by hardness versus the percentage of added accelerator.

EXPERIMENT 9

PREPARATION OF A PHENOL-FORMALDEHYDE WATER-SOLUBLE CONDENSATION PRODUCT

Varnish Preparation

In a suitable three-necked flask fitted with mechanical stirrer, thermometer, and a reflux condenser and heated by means of a suitable bath (120 ± 5° C) place 376 grams (4 moles) of phenol and 420 grams of 37.2% formalin (5.2 moles of formaldehyde). Catalyze the reaction with 3.2 grams of sodium hydroxide dissolved in 20 cc of water. Allow the reaction to proceed with stirring for 45 minutes after the beginning of reflux. Immediately at the end of 45 minutes, cool the reaction by immersing the flask in a bath of cold water. Bottle the product, label, and save for determinations and future experiments. Store in a refrigerator.

Tests

Part A. Carry out the following determinations on the above product:

	Test Method	*Results*
Formaldehyde	1	....
Specific gravity	6	....
Viscosity	7	....
Stroke cure	4	....
*p*H	8	....

Test its solubility in the following solvents:

	Solubility
Water	....
Alcohol	....
Acetone	....
Ethylene glycol	....
Dioxane	....

Part B. To individual 10-cc samples of the above product, add one of each of the following substances in the quantity indicated. Determine the *p*H and stroke cure time at 130° C on a portion of each of the above samples and save the remainder to determine the stability of the syrups. Observe these stored samples at the end of two weeks and note whether precipitation has occurred.

Samples	*Substances Added*	*pH*	*Cure Time*	*Description of Film*	*Stability*
1	1 cc of 10% lactic acid	....	....	....	....
2	1 cc of 5% oxalic acid	....	....	....	....
3	1 cc of 5% sulfuric acid	....	....	....	....
4	1 cc of 3% sulfuric acid	....	....	....	....
5	1 cc of 5% sodium hydroxide	....	....	....	....
6	1 cc of 10% ammonium hydroxide	....	....	....	....
7	0.1 gram of hexamethylenetetramine	....	....	....	....
8	0.1 gram of calcium hydroxide	....	....	....	....
9	Control sample, no addition	....	....	....	....

QUESTIONS

1. Why does this resin cure readily?
2. Write a brief discussion of the data obtained from the series of experiments in Part *B*.

Suggested Extensions

1. Since many industrial water-soluble resins with special properties are made by replacing phenol with its homologues, determine what percentage of *o*-, *m*-, or *p*-cresol, or a mixture of these, can be substituted for the phenol before the reaction product loses part or all of its water solubility. Plot whatever data are obtained against the mole fraction or percentage of phenol replaced.
2. The acetone solubility test measures the rate of cure of a varnish solution and is used industrially as a control method in the preparation of laminated stock. This test (Test Method 10) should be performed on this varnish if time permits. Record and graph the results to observe the nature of the cure curve.

Cure Time	*Percentage of Acetone Solubility*
0	....
5	....
10	....
15	....
20	....
30	....

EXPERIMENT 10

PREPARATION OF A PHENOL-FORMALDEHYDE SPIRIT-SOLUBLE LAMINATING VARNISH

Varnish Preparation

A special resin flask is used to permit ready removal of the resin, if, through accident, the resin becomes cured during the reaction or during dehydration. In such a resin flask, fitted with a mechanical stirrer, thermometer, and reflux condenser and heated by immersion in a suitable bath (Figure 2) to a temperature of 120 ± 5° C, place 188 grams (2 moles) of phenol and 177 grams (2.2 moles) of formaldehyde. Catalyze the reaction with 15 grams of concentrated (28%) ammonium hydroxide solution. Allow the reaction to proceed at reflux. A cloudy two-layer system usually appears in 17 to 25 minutes. At the end of 40 minutes of refluxing, cool the resin by immersing the flask in a bath of cold water. Dehydrate immediately by one of the following two methods. Either may be used, though the products formed will differ somewhat from each other. The vacuum method is the preferred industrial method.

Method 1—Vacuum Dehydration

Convert the resin flask to a dehydration system by using a single-necked dome as the resin flask cover (Figure 3). Arrange a condenser and receiver as shown in Figure 3. Remove the water from the resin under a pressure of 25 mm or less, using a bath temperature of 120 ± 5° C until the internal temperature of the resin being dehydrated rises to 80° C. Plot time-temperature of dehydration curve for your data, taking temperature readings at 10-minute intervals at the beginning of dehydration and shortening that interval as dehydration progresses.

Time	*Temperature*
10 minutes	....
20 minutes	....
30 minutes	....
35 minutes	....
40 minutes	....
42 minutes	....
etc.	....

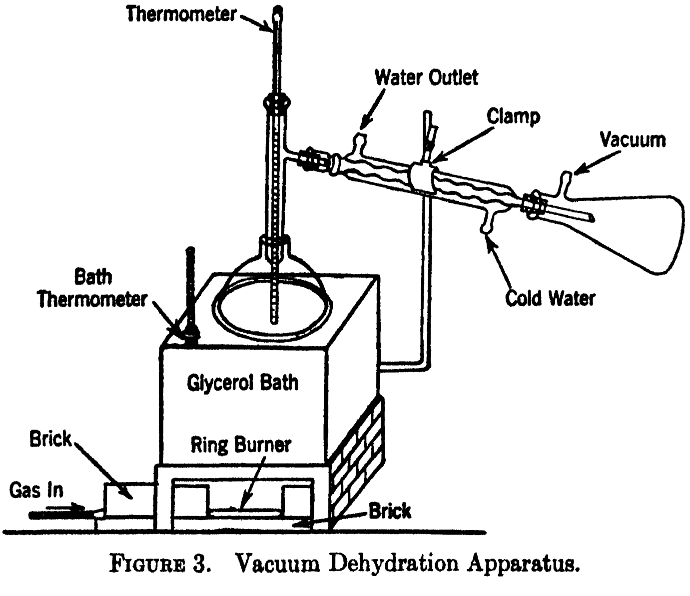


FIGURE 3. Vacuum Dehydration Apparatus.

The approximate time of dehydration is 45 minutes. Observe the resin closely as the resin temperature approaches 80° C. When the temperature is 80° C, *turn out all flames* and break the vacuum system, and, with stirring, add 1.2 grams of stearic acid. Maintain the resin hot by leaving the resin flask immersed in the bath. To the warm resin add 125 cc of a mixture of alcohol and toluene in 90 to 10 ratio by volume and remove the resin flask from the bath and cool to room temperature. Determine the resin content and the weight of the resin solution. Adjust the varnish to 50% solids with additional alcohol-toluene solvent as needed. Determine the stroke cure of the varnish. Bottle and label the product, and save for future use in Experiment 11.

Method 2—Open-Boil-Down Dehydration

Using an open iron or aluminum pan, under a well-ventilated hood and over the free flame of a Bunsen burner, boil down the resin *until it becomes clear* (i.e., the two-phase system disappears) and all the water has been distilled off. It is best to stir the boiling resinous mixture mechanically and slowly. Keep a thermometer immersed in the resin during the dehydration and note the temperature at which the resin becomes clear. *When the resin becomes clear, add 1.2 grams of stearic acid.* Continue stirring and boiling slowly until the temperature of the resin reaches 105° C. Shut off all flames and allow the material to cool to 80° C. Dilute the resin with 125 cc of a mixture of alcohol and toluene in a 90 to 10 ratio. Determine the resin content and the weight of the resin solution. Adjust the varnish to a 50% resin solids with the alcohol-toluene solvent. Determine the stroke cure of the resin, bottle, and label the product, and save for future use in Experiment 11.

Suggested Extensions

1. Prepare two batches of varnish and dehydrate the lots by the different methods. Dilute to 50% solids and make a comparison of the resulting products by carrying out the following determinations:

	Open-Boil-Down Dehydration	*Vacuum Dehydration*
Stroke cure	....	....
Viscosity	....	....

	Percentage of Acetone Solubility	
Cure Time	*Open-Boil-Down Dehydration*	*Vacuum Dehydration*
0	....	....
5	....	....
15	....	....
20	....	....
30	....	....

2. The properties of the varnish, such as viscosity, rate of cure, and type of cure, are determined to a great extent by the nature of the phenolic bodies used for the reaction with formaldehyde. In the manufacture of industrial laminates, many types of mixtures are used, particularly the cresol and xylenol fractions. The following mixtures are worthy of investigation, using one mole of total phenolic body to 1.1 moles of formaldehyde.

Type Mixture			
1	Phenol 81–85%	*o*-Cresol 3–5%	*m-p*-Cresols 10–16%
2	Phenol 81–85%	*o*-Cresol 11–14%	*m-p*-Cresols 1–8%
3	Phenol 40–50%	*m-p*-Cresols 10–15%	Xylenols 40–50%
4	Phenol 12–15%	*o*-Cresol 43–45%	*m-p*-Cresols 45–48%

EXPERIMENT 11

PREPARATION OF A PHENOL-FORMALDEHYDE LAMINATING STOCK

General Procedure

The first step in the preparation of a laminated panel comprises preparing the laminae or the individual layers from which the panel is constructed. The most common method consists of impregnating continuous sheets of paper or cloth, etc., with a solution of the resin and thereafter eliminating the solvent from the impregnated sheet, leaving a uniformly dispersed resin in the base material. For the purposes of this experiment two types of paper will be used.

Paper A—Rag Paper

This type of paper represents an electrical-grade, high-quality, highly absorptive sheet. It is used in the preparation of solid panels, i.e., core as well as surface or face sheets, such panels possessing excellent electrical properties. For non-electrical or for decorative panels, rag paper is used only for the surface or face of the panel on a core of impregnated lower cost paper. In many cases pigmented rag papers and dyed varnishes are used for the preparation of the face sheets.

Paper B—Kraft Paper

This paper represents a low-cost bleached kraft paper and is used primarily in core construction impregnated with a low-cost resin. When used by itself without face sheets, it produces low-cost low-quality laminated panels. For decorative panels, it is faced with higher quality surface sheets which are impregnated with phenolic resins for the dark colors and with urea or melamine resins for the pastel shades.

Impregnated Sheets

The paper to be impregnated is cut into sheets 7 by 13 inches so that, after impregnation and drying, they can be recut to 6 by 6 inches for future use in the pressing operation. Cut 18 sheets each of papers *A* and *B* to a 7 by 13 inch size for dipping in the laminating syrups. Dipping consists of running the paper very slowly and at a constant rate through the laminating varnish, allowing it to pick up the proper amount of resin. The resin is deposited on both sides of the paper by drawing the paper under the surface of the resin solution. For convenience in dipping, the paper can be held at one end by two paper clips and pulled through the resin solution.

After being dipped, the impregnated sheets are dried to a predetermined minimum and maximum volatile content. The resin content (Test Method 11) of the treated paper depends on the viscosity and the resin content of the varnish and the absorbency of the paper being treated. Increased resin content can be obtained by dipping, partially drying, and then redipping as many times as necessary to obtain the desired resin content on the paper. An effort should be made to have 50% resin in the treated stock of this experiment

(Test Method 11). Dip nine sheets of each of the two papers in the water-soluble and nine of each in the spirit-soluble varnishes of Experiments 9 and 10 respectively.

After dipping them, allow the samples to air-dry for 30 minutes and then dry in an air-circulating oven at 110° C until the volatile content (Test Method 11) is 6 ± 2%. The approximate drying time is to be recorded in the table below. Use one sheet to obtain the control data required for this table. The sheet stock code or number consists of two symbols. The first symbol is a number and indicates the resin used; the second is a letter and indicates the type of paper used. Thus sheet stock 9*A* indicates that the water-soluble resin of Experiment 9 was used and that the paper impregnated was paper *A* or a rag paper.

Record of Data

Resin of Experiment	*Paper*	*Sheet Stock Number*	*Number of Sheets*	*Weight Paper*	*% Resin*	*Approximate Drying Time at 110° C*	*% Volatile Content*
9. Water-soluble	*A*	9*A*	9	....	....	....	....
9. Water-soluble	*B*	9*B*	9	....	....	....	....
10. Spirit-soluble	*A*	10*A*	9	....	....	....	....
10. Spirit-soluble	*B*	10*B*	9	....	....	....	....

Black or colored stocks may be obtained either by adding dye to the varnish or by using suitably dyed or pigmented paper stock.

Paper Tests

Cut 2-inch squares of each type of paper and drop flat on the surface of the varnishes. Note any difference in time for the varnish to penetrate through to the surface of the two papers. If no difference is found, repeat the test, using a light mineral oil instead of the varnishes.

QUESTIONS

1. What do you believe the "volatile content" measures?
2. If the water or alcohol content of a treated stock were determined by drying a sample in a desiccator over phosphorus pentoxide, would this value be lower than the "volatile content" value? Why?
3. What would be the effect of drying the paper before impregnating with varnish?
4. Explain the differences between the two papers observed in the paper tests.

EXPERIMENT 12

PREPARATION OF LAMINATED PHENOLIC PANELS

Laminating consists of bonding together as laminae a number of resin-impregnated sheets under heat and pressure to form a panel which fuses together more or less permanently, depending on the resin used and other conditions in its preparation.

Cut the 13 by 7 inch treated stock of Experiment 11 into 6 by 6 inch sheets. In trimming, remove those edges which show an accumulation of excess resin as a result of dripping and draining during the impregnation and drying process. Prepare the five panels from the cut stock according to the build-up indicated below.

Panel	*Panel Build-up*
I	8 sheets of stock 9*A* (water-soluble varnish)
II	8 sheets of stock 9*B* (water-soluble varnish)
III	8 sheets of stock 10*A* (spirit-soluble varnish)
IV	8 sheets of stock 10*B* (spirit-soluble varnish)
V	1 sheet of stock 10*A* (spirit-soluble varnish) 6 sheets of stock 9*B* (water-soluble varnish) 1 sheet of stock 10*A* (spirit-soluble varnish)

Pressing Operation

Start with a cold, laminating press. On the bottom platen place two or three sheets of kraft paper, which will both act as an equalizing pad and serve to collect any resin drippings or squeeze-out. Next place on the kraft paper either a dull satin-finished or polished metal plate or pan which has been previously dusted with zinc stearate. On this place (1) the laminating stock required for the panel build-up, (2) another metal plate, and (3) two or three sheets of kraft paper. Close the press on the panel, applying about 1100 to 1300 pounds per square inch pressure and maintain that pressure throughout the laminating process. Heat the platens to 140° C and maintain the pressing at that temperature for 35 minutes. Cool the press platens to room temperature, release the pressure, and remove the laminated panel. The press pan or plates should be of slightly smaller dimension than the 6 by 6 inch treated stock to permit resin to squeeze out and for easy removal

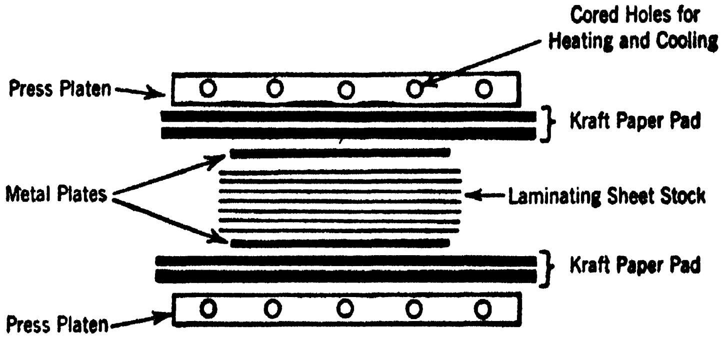


FIGURE 4. Single-Panel Build-up.

of the laminated panel. The press and panel build-up for a single panel and for multiple panels are given in Figures 4 and 5 respectively. When multiple panels are prepared in a single press opening, thermocouples should be used in between the intermediate panels to determine that the center panels have received heat for a sufficient time.

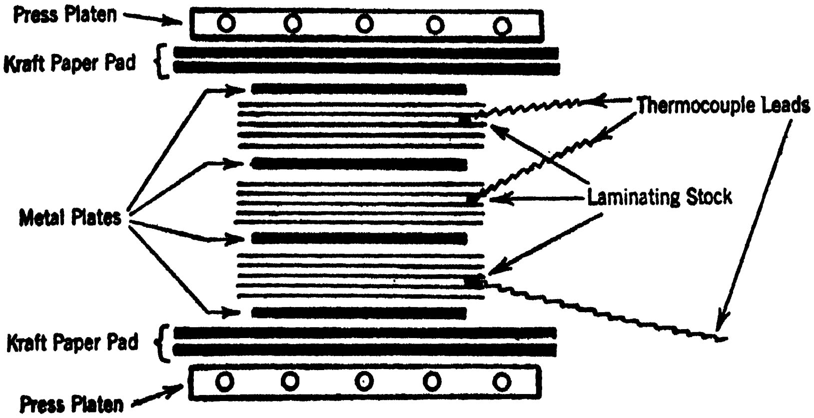


Figure 5. Multiple-Panel Build-up.

QUESTIONS

1. What is the purpose of the zinc stearate dusting? Is it necessary with the use of a spirit-soluble varnish?
2. Break a panel at one corner. Is it uniform and well bonded?
3. What is the condition of the finished panel if the volatile content is too low; if the volatile content is too high?

Suggested Extensions

1. Consult N.E.M.A. Laminated Phenolic Products Standards and list the standard grades of laminated plates, tubes, and rods available.
2. Determine the effect of resin content on the physical properties of a finished laminated panel. Maintain either the paper or the fabric base constant and vary the resin between 30 and 60% in 5% intervals.
3. Consult A.S.T.M. Standards for determining the following physical properties:
   - *a.* Impact strength
   - *b.* Flexural strength
   - *c.* Tensile strength
   - *d.* Dielectric strength
   - *e.* Compressive strength
   - *f.* Bonding strength
   - *g.* Water absorption
4. Compare a paper-base laminated panel to a fabric-base laminated panel.
5. Study the effect of the type of weave or the thickness of a fabric in a laminated product.
6. Study the effect on the properties of finished panels made with face sheets having a high resin content and fillers having a low resin content by varying the resin content of the face sheet and holding the resin content of the filler constant.

EXPERIMENT 13

PREPARATION OF ACID-CATALYZED PHENOL-FORMALDEHYDE MOLDING RESINS

Part A. Phenol Resin

In a suitable resin flask (Figure 2) fitted with a thermometer, reflux condenser, and stirrer, place 188 grams (2 moles) of phenol and 135 grams of formalin (1.67 moles of formaldehyde). Catalyze the reaction by the addition of 0.6 gram of concentrated sulfuric acid dissolved in 20 cc of water. An exothermic reaction takes place either upon addition of the catalyst or upon application of a small amount of heat. Allow the reaction to proceed as long as it is exothermic, but as soon as it slows down, keep it at reflux by immersion in a 110° C bath. At the end of an hour of reflux and without cooling the resinous mass add the approximately calculated amount of calcium hydroxide dispersed in 5 cc of water necessary to neutralize the sulfuric acid catalyst and stir for 3 minutes. The water layer should test neutral to litmus. If it is still acid, adjust to neutrality with a little more calcium hydroxide. Remove the stirrer and convert the flask to a distillation system (Figure 3). Dehydrate the reaction mixture under a pressure of 100 mm while it is being heated in a bath at 120 to 130° C until a sample of the resin is brittle when removed from the reaction vessel and cooled. Collect the water and report the following data:

Water Collected

Actual		*Theoretical*	
		H_2O in sulfuric acid	.... grams
		H_2O in formalin	.... grams
		H_2O in lime	.... grams
		H_2O of condensation	.... grams
Total grams	.... grams	Total grams	.... grams

The internal temperature of the resin as measured by the thermometer at the completion of dehydration should be at about 80° C. The thermometer must be immersed in the resin during the dehydration. Next pour the resin into a metal cooling pan and allow the resin to cool to room temperature. Break up the cooled resin, and bottle and label it. Test its solubility in acetone, alcohol, benzene, and toluene. This resin will be used in preparation of a phenolic molding resin and a phenolic molding powder.

Part B. *o*-Cresol Resin

Using the same equipment as in Part *A*, react 108 grams (1 mole) of *o*- or *p*-cresol with 62.5 grams of formaldehyde (0.835 mole) and 0.3 gram of concentrated sulfuric acid in 10 cc of water. React for one hour, neutralize, and dehydrate as in Part *A*. Bottle and label the resin for future use and tests.

Part C. Butylphenol or Amylphenol Resin

Using the same equipment as in *A* and *B*, react either 150 grams (1 mole) of *p-tert*-butylphenol or 164 grams (1 mole) of *p-tert*-amylphenol with 62.5 grams of formalin and 0.3 gram of sulfuric acid in 10 cc of water. Neutralize with lime, etc., and treat as in Part *A*, saving the resin product for future use and tests.

Tests

In a mortar grind together 5 grams of each of the above samples with 0.5 gram of hexamethylenetetramine and determine the stroke cure at 150° C on the hot plate. Remove the films from the hot plate after 3 minutes, test their solubility in acetone, and compare with the original uncured samples.

Sample	*Original Solubility in Acetone*	*Cure Time at 150° C*	*Condition at 3 Minutes at 150° C*	*Solubility After Curing*
Resin 13*A*	....	....	....	....
Resin 13*B*	....	....	....	....
Resin 13*C*	....	....	....	....

QUESTIONS

1. Write what you believe to be the chemical formula of the phenol-formaldehyde resin if the average molecular weight is about 600? 900? Is it soluble in alcohol, benzene, toluene, acetone, dioxane?
2. Why is less than one mole of formaldehyde per mole of phenol used in the preparation of a soluble fusible resin?
3. Why is the acid catalyst neutralized?
4. Explain the differences in the curing properties of resins 13*A*, 13*B*, and 13*C*.
5. Write the structural formulas of resins 13*A*, 13*B*, and 13*C*.

Suggested Extensions

1. Determine the rate of formaldehyde consumption.
2. Vary the ratio of phenolic body to the aldehyde.
3. Investigate other acid catalysts such as hydrochloric acid and oxalic acid.
4. Plot the graph of the temperature of the resin versus the time of dehydration in an experiment in which the bath temperature and pressure are maintained constant.
5. Study the change in the flow point of resin with respect to the time and also to the temperature as dehydration progresses.
6. Study the change in flow point and viscosity of the resin in alcohol solutions as part or all of the phenol is replaced by cresols and/or xylenols.
7. Study the varying mole ratios of phenol to a *p*-substituted phenol and plot the cure properties versus the mole fraction of the phenol.

EXPERIMENT 14

PREPARATION OF A CURING PHENOLIC MOLDING RESIN

The components, indicated in the ratios below, are blended together and pulverized either in a mortar, a grinder, or a ball mill until they pass through a 100-mesh screen. The amount of resin available from the previous experiment will determine the amount of molding resin to be prepared. A portion of resin 13*A* must be saved for Experiment 20.

Resin from Experiment 13*A*	100	parts by weight
Hexamethylenetetramine	10	parts by weight
Lime	1.5	parts by weight
Calcium stearate	0.2	part by weight

Sticking and packing may occur during grinding, and the degree to which they are encountered will be dependent somewhat on the flow point of the resin. Therefore, no definite time for processing can be set. Approximately 15 minutes of ball milling, however, should be sufficient. After screening the material, weigh the resin; bottle, and label. Determine the stroke cure (Test Method 4) of the finished resin at temperatures of 110 to 180° C in 10-degree steps and graph the cure time versus the temperature.

QUESTIONS

1. What is the purpose of: (*a*) the hexamethylenetetramine, (*b*) the lime, (*c*) the calcium stearate?
2. How does the cure time change with the temperature?

Suggested Extensions

1. With respect to the phenol resin vary the ratios of (*a*) the hexamethylenetetramine and (*b*) the lime. Plot (*a*) the cure time versus the composition; (*b*) the cure time versus the temperature; and (*c*) the acetone extraction versus hexamethylenetetramine and lime contents.
2. Describe the nature of the cured films as the composition is changed.
3. Why does reduced hexamethylenetetramine give rubbery cures?

EXPERIMENT 15

PREPARATION OF A PHENOLIC MOLDING POWDER

With the molding resin of Experiment 14, prepare two lots of molding powder, using the amounts and components indicated below:

Compound 1	*Parts by Weight*
Resin of Experiment 14	45
Filler (wood flour, plastic grade)	55
Color (nigrosine)	2% by weight of (resin plus filler)
Lubricant (calcium stearate)	0.5% of total weight

Compound 2	
Resin of Experiment 14	30
Filler (asbestos, plastic grade)	70
Color (nigrosine)	2% by weight of (resin plus filler)
Lubricant (calcium stearate)	0.5% of total weight

Blend the resin, filler, color, and lubricant either in a change-can mixer or in a tumbling barrel. Sheet the blended ingredients on differential rolls or rubber mill for 60 to 90 seconds, the front roll being heated with 15 to 20 pounds of steam, the rear roll being maintained cold with running water. The final sheet should leave the rolls cleanly in the form of a continuous sheet, and it should have a shiny appearance on the inside and a crinkly appearance on the outside. Experience will be necessary to determine the proper amount of sheeting time to obtain the desired flow in the molding powder since longer processing decreases the plastic flow of the compound. The sheet becomes brittle when cool and is easily ground. The molding powder will be used in the next experiment.

QUESTIONS

1. Why is less resin used in the asbestos compound?
2. Is the resin absorbency of asbestos less than that of wood flour?

Suggested Extensions

1. Vary the ratio of resin to filler, and correlate the properties of the final molded piece to its composition.
2. Vary the nature of the filler, e.g., alpha flock, cotton flock, and chopped fabric, and study the effect on the finished molded product.
3. Compare the properties of an unmilled powder with a milled and ground molding powder.

EXPERIMENT 16

PREPARATION OF A PHENOLIC MOLDED ARTICLE

Using the molding powders from Experiment 15, prepare three molded test pieces from each compound. Carry out the molding by compression in any suitable mold and hydraulic press with either steam or electrically heated molds. Use a molding pressure of 2000 to 2500 pounds per square inch and a cure time of 5 minutes at 160 to 165° C. Eject the molded piece from the mold hot, i.e., without cooling of the mold. Determine water absorption (Test Method 13), boiling water resistance (Test Method 14), and specific gravity (Test Method 15) of the samples. Compare the heat resistance of the wood-flour- and the asbestos-filled material by placing the molded pieces in an oven for 15 minutes each at the following successively higher Centigrade temperatures: 175°, 185°, 195°, 205°, 215°, 225°, etc., until blistering occurs and record that temperature together with the other data in the table below.

	Compound 1 (Wood Flour)	*Compound 2 (Asbestos)*
Water absorption	....	....
Specific gravity	....	....
Heat resistance (temperature °C)	....	....

QUESTION

1. Explain the difference in the heat resistance of the two compounds. Of what importance is this difference commercially?

Suggested Extensions

1. Consult the A.S.T.M. Standards and, using suitable molds, prepare test specimens for all physical and electrical properties, e.g., impact, flexural, compressive, and tensile strengths, the modulus of elasticity, resistance to solvents, alkalies, and acids.
2. Investigate the effect of cure times at a series of temperatures as regards the development of the maximum properties of the molding compounds.
3. Correlate the acetone solubility of a molded specimen with the time of cure, first at one temperature. e.g., at 150° C, then at higher temperatures, e.g., 160° C and 170° C.

EXPERIMENT 17

PREPARATION OF PHENOL-FURFURAL RESIN

In a resin flask react 94 grams (1 mole) of phenol, 120 grams (1¼ moles) of furfural, and 2.4 grams (0.06 mole) of sodium hydroxide in 10 cc of water for 2½ hours at reflux temperature. Then dehydrate the reaction product under a pressure of 100 mm to a solid brittle fusible resin (Figure 3). The internal temperature will be higher than for a phenol-formaldehyde resin. The student will determine the dehydration conditions. After determining, by the hot plate test, the suitable amount of hexamethylenetetramine and lime necessary to cure the resin, prepare a molding compound, using 50 parts of resin and 50 parts of wood flour as a filler, together with the proper amount of lime and hexamethylenetetramine as determined above experimentally. Compare this compound in all phases to the phenol-formaldehyde resins of Experiments 13, 14, 15, and 16. Note particularly the prolonged viscous condition of the resin before a complete cure is accomplished and that a longer cure time may be required than in the ordinary phenol-formaldehyde resins.

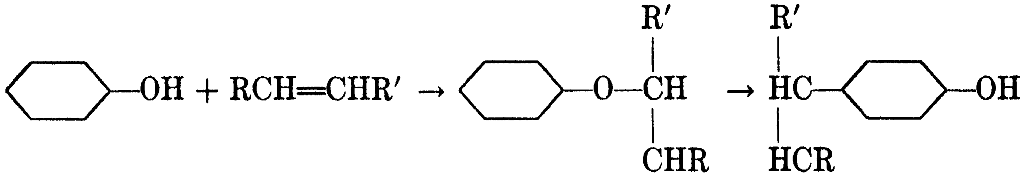
QUESTIONS

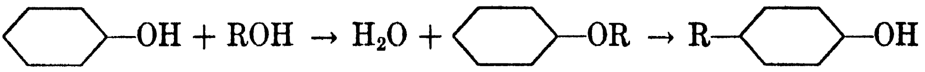
1. Discuss the differences in the reactivity of formaldehyde and furfural with phenol. Is more catalyst required in one case than in the other? Can a sodium hydroxide-catalyzed phenol-formaldehyde resin be dehydrated easily to a solid, brittle resin without neutralization?
2. Of what importance is the prolonged flow time of the furfural resins to the industrial manufacturer and user?

EXPERIMENT 18

PREPARATION OF SUBSTITUTED PHENOLS

If the substituted phenols required for Experiment 19 are not available, they may be prepared in the following ways. One synthesis uses an unsaturated compound for the addition to phenol; another uses an alcohol in the preparation. It is most probable that both these reactions proceed through an ether intermediate which rearranges as follows:





Part A. The Preparation of Styrylphenol

Materials

Phenol (dry—2 moles)	188 grams
Styrene (1 mole)	104 grams
Sulfuric acid (concentrated—0.1%)	0.3 gram
Inhibitor for styrene (sulfur or copper powder or copper acetate)	0.5 gram

Procedure. Into a three-necked flask equipped with a stirrer, reflux condenser, thermometer, and dropping funnel introduce the dry phenol, sulfuric acid, and inhibitor, and heat to reflux at about 170 to 172° C. Then slowly drip in the styrene at the rate of about 70 drops per minute, and keep the reaction under reflux and agitation. Continue heating at reflux for 30 minutes after the final addition of the styrene. To the hot reaction mixture add 0.5 gram of calcium hydroxide dispersed in 20 cc of H_2O to neutralize the sulfuric acid. Distill the reaction mixture at atmospheric pressure to recover 1 mole of phenol (b.p. about 180° C) until the vapor temperature begins to drop momentarily, indicating that the bulk of the phenol has distilled. The residual styrylphenol is distilled under vacuum. The boiling point of styrylphenol at 30 mm is 210 to 240° C; at 20 mm it is 198 to 210° C. In a liquid composition the material is about 90% *p*-styrylphenol and 10% *o*-styrylphenol. When made in small lots the yield is about 85%; in large lots it is about 95%. If desired, the ortho and para derivatives can be separated by suitable fractionation and recrystallization.

Part B. The Preparation of *p-tert*-Amylphenol

In a dry, 2-liter, three-necked flask equipped with a mechanical stirrer, reflux condenser, and thermometer, place 88 grams of tertiary amyl alcohol, 118 grams of phenol, and 125 cc of petroleum ether. While stirring, add progressively, and in small quantities, 67 grams of anhydrous aluminum chloride, keeping the temperature of the mixture below 20° C. The aluminum chloride is added from a shaker over a period of 1 to 1½ hours. The shaker is prepared by fitting a bottle with a cork pierced by a 10-cm section of 10-mm glass tubing, which is in turn fitted with a small cork stopper. To add the aluminum chloride, remove the cork from the shaker and the thermometer from the reaction flask and shake into the flask a few grams of the aluminum chloride. Evidence of reaction is found in the liberation of hydrogen chloride and the fact that the reaction mixture turns a deep red. The amount of aluminum chloride added is determined by weight difference. Stir the reaction mixture for 1 hour after all the aluminum chloride has been added. Pour the reaction mixture into a beaker containing 150 grams of ice and 150 grams of concentrated hydrochloric acid. Extract the resulting material three times with 100 cc of ethyl ether per extraction. Dry the ether extract over anhydrous sodium sulfate, filter, and, *using proper precautions of avoiding flames, etc.*, remove the ether by distillation. Distill the residue, using an air condenser, collecting the fraction boiling from 210 to 270° C. Redistill and collect a fraction boiling from 250 to 265° C. This fraction should crystallize upon cooling and can be recrystallized from petroleum ether. The yield of *p-tert*-amylphenol (m.p. 94 to 95° C) should be 80 to 90% of the theoretical.

Suggested Extension

1. Prepare a series of *p*-substituted phenols of the formula R—C_6H_4OH, where R is a methyl, ethyl, propyl, butyl, or amyl group, and save for Experiment 19 to determine the minimum chain length necessary to achieve solubility in drying oils.

EXPERIMENT 19

PREPARATION OF OIL-SOLUBLE SUBSTITUTED PHENOL DIALCOHOLS

Part A. Preparation of Dialcohols

In a suitable resin flask react at least one of the following groups of materials:

Group I		*Group II*		*Group III*	
tert-Butylphenol	140 grams	*tert*-Amylphenol	154 grams	Styryl phenol *	197 grams
Formalin	165 grams	Formalin	165 grams	Formalin	165 grams
NaOH in 10 cc of water	2 grams	NaOH in 10 cc of water	2 grams	NaOH in 10 cc of water	2 grams

* Phenylphenol may be used in place of styrylphenol.

Reflux the materials for 2 hours and cool to room temperature. Neutralize the mixture with 5% acetic acid solution and wash thoroughly with water by decantation. Dehydrate the oily layer under reduced pressure, but do not allow the temperature of the dialcohols to rise above 35° C until all the free water is removed. Break the vacuum system and remove about half the dialcohols, bottle, label, and save for future use. Leave the remainder of the dialcohols in the resin flask for dehydration to a solid resin.

Part B. Solid Oil-Soluble Resin

The dialcohols in the resin flask are converted to solid resins by continued dehydration at 20 to 30 mm pressure and by allowing the temperature of the dehydrating mass to rise slowly until a test sample of resin is obtained which is solid at room temperature. Discoloration of the resin may occur if temperatures in excess of 80 to 85° C are used. Pour the dehydrated resin while still hot into cooling pans, allow to cool, break up, bottle, label, and save for future use.

Suggested Extension

1. Prepare resins with formaldehyde from the *p*-substituted phenols of Extension 1, Experiment 18.

EXPERIMENT 20

COMPARISON OF THE OIL SOLUBILITY OF PHENOL RESINS

Oil Solubility

Determine the oil solubility (Test Method 16) of the resins from the experiments listed below, in the following oils:

Oil	13*A* *Acid Phenol Formaldehyde*	13*B* *Acid Cresol Formaldehyde*	13*C* *Acid Butylphenol or Amylphenol Formaldehyde*	19*A* *Dialcohol*	19*B* *Dialcohol Resin*
Tung	....	....	....	....	....
Oiticica	....	....	....	....	....
Perilla	....	....	....	....	....
Linseed	....	....	....	....	....
Castor	....	....	....	....	....

Solvent Solubility

Determine the solubility of the same resins in the following paint and lacquer solvents:

Solvent	*Resin*				
	13*A*	13*B*	13*C*	19*A*	19*B*
Toluene	....	....	....	....	....
Solvent naphtha	....	....	....	....	....
Butyl acetate	....	....	....	....	....
Acetone	....	....	....	....	....
Alcohol	....	....	....	....	....
Methyl ethyl ketone	....	....	....	....	....

QUESTIONS

1. Is a resin that is soluble in hydrocarbon solvents necessarily soluble in oils?
2. Discuss oil solubility relative to the length of the substituted chain on the phenol.
3. Why would you expect the phenol dialcohols to be more reactive than the methylene compounds prepared under acid conditions?

EXPERIMENT 21

PREPARATION OF AN AIR-DRYING, OIL-SOLUBLE PHENOLIC VARNISH

Dissolve 20 grams of resin from Experiment 19, Part *B*, in 40 grams of tung oil in a wide-mouthed beaker heated to 100° C. After the resin has dissolved, and foaming has ceased, raise the temperature of the mixture slowly to 220 to 230° C, and maintain it at that temperature until a 6–8-inch vertical string is obtained. This test is performed by placing a small sample of the hot resin on a glass plate, allowing the resin to cool to approximately room temperature, touching the flat side of a cool spatula to the resin, and withdrawing the spatula. The distance to which the thread of resin can be drawn before breaking is known as the string length. When a 6–8-inch string is obtained, *shut off all flames*, and allow the reaction mixture to cool to about 160 to 170° C. Dilute the resinous product with 100 cc of solvent, consisting of a mixture of toluene and 70-degree naphtha in the ratio of 25 to 75 parts. Allow the varnish to cool to room temperature and determine its specific gravity before adjusting the specific gravity of the varnish to approximately 0.83 by the addition of the proper amount of hydrocarbon solvent mixture. About 150 cc of varnish is obtained. Divide the varnish into three equal parts and treat as follows:

Varnish 1. Use as prepared.
Varnish 2. Add 0.15 gram of a naphthenate drier.
Varnish 3. Add 0.75 gram of a naphthenate drier.

The drier can be lead, cobalt, or magnesium naphthenate, or a mixture of these driers. Mix each lot well, deposit films on glass plates by flowing a sample of the varnish over the glass, and allow to drip vertically. Prepare two plates from each varnish lot, one to be air-dried at room temperature (*a*) and the other (*b*) to be baked in an oven at 150° C.

Record of Data on Drying

		Air-Dried			*Baked*	
Varnish	1*a*	2*a*	3*a*	1*b*	2*b*	3*b*
Freedom from tack (time)	....	....	....	....	....	....
Hard and dry (time)	....	....	....	....	....	....
Type of film	....	....	....	....	....	....

Immerse the dried films in boiling water and note the time necessary for the films either to become opaque or to peel from the glass. Note the order of decreasing resistance to boiling water.

QUESTION

1. What is the effect of the addition of a drier, and how is it changed by the quantity of the drier?

Suggested Extensions

1. Investigate the relation between the length of string and the time to air-dry.
2. Investigate the effect of different ratios of resin to oil.
3. Investigate the gelation time of a drying oil (Test Method 18) as affected by small and large amounts of oil-soluble phenolic resin.
4. Compare a series of varnishes in which the drying oil, e.g., tung oil, has been replaced in part by other natural and synthetic drying or semi-drying oils.

EXPERIMENT 22

PREPARATION OF METHYLOL DERIVATIVES OF UREA

Preparation of Monomethylolurea

Dissolve 0.4 gram of barium hydroxide in 20 cc of water, and, at room temperature, dissolve 24 grams of urea in this alkaline solution. Cool the solution in an ice bath and, drop by drop, add 0.4 mole of formaldehyde, using the calculated volume of formalin. When the formaldehyde content is substantially zero, as determined by the bisulfite titration method (Test Method 2), precipitate the barium as the carbonate by bubbling gaseous carbon dioxide through the solution. Filter the solution free of the barium carbonate, and evaporate the filtrate to dryness under reduced pressure and at 30 to 40° C. Dry the crystalline mass completely in a vacuum desiccator over anhydrous sodium sulfate. Yield .... grams.

Melting Point	*Found*	*Literature*
Monomethylolurea	....	....

Solubility Tests

Test the solubility of monomethylolurea, using one part of the monomethylolurea to ten parts of solvent in the following solvents at room temperature. If no solution is effected, heat to reflux. If solution occurs on refluxing, determine whether precipitation occurs on cooling.

		Solubility	
Solvent	*Room Temperature*	*Reflux*	*Reprecipitation*
Water	....	....	....
Ethyl alcohol	....	....	....
Butyl alcohol	....	....	....
Glycol	....	....	....
Acetone	....	....	....
Ethyl acetate	....	....	....
Benzene	....	....	....

Resinification of Monomethylolurea

Heat a sample of monomethylolurea on a 130° C hot plate for 5 minutes alone, as a control. Also heat other portions with a very small amount of each of the indicated substances previously blended by grinding in a mortar. Note whether formaldehyde is liberated during the heating.

Sample	*Result of Cure*	*Water Resistance of Film*
Monomethylolurea	....	....
Monomethylolurea plus small amount of ethylenediamine	....	....
Monomethylolurea plus small amount of hexamethylenetetramine	....	....
Monomethylolurea plus small amount of phthalic anhydride	....	....

Note the effect of the addition agent on the curing of the sample. Remove the film from the hot plate with a scraper and test its resistance to water by immersing it in a container of water.

Preparation of Dimethylolurea

Using 0.1 *N* sodium hydroxide, adjust the acidity of 40 cc of formalin until it is just basic to litmus. Buffer the solution with 0.2 gram of monosodium phosphate. Determine the formaldehyde content of this solution, and, using the calculated volume of buffered formalin, react the ingredients in the ratio of 0.21 mole of formaldehyde to 0.1 mole of urea for 15 hours by dissolving the urea in the buffered solution of formaldehyde. Filter off the white precipitate, wash dry with anhydrous ethyl alcohol, and vacuum-dry at 30 to 35° C. Record the melting point of the dimethylolurea.

Melting Point

Found ....° C Literature ....° C

Solubility Tests

Test the solubility of dimethylolurea in the following solvents at room temperature. Repeat the solubilities at the reflux temperature of the solvent. Cool the refluxed mixture to room temperature and note if any precipitation occurs. If not, explain.

	Solubility		
Solvent	*Room Temperature*	*Reflux*	*Reprecipitation*
Water	....	....	....
Ethyl alcohol	....	....	....
Butyl alcohol	....	....	....
Glycol	....	....	....
Glycerol	....	....	....
Acetone	....	....	....

Resinification of Dimethylolurea

On a hot plate at 130° C heat a small sample of dimethylolurea alone as a control. Also heat additional portions with a very small amount (approximately 1% the weight of the urea) of each of the following indicated substances, previously blended with the dimethylolurea by grinding in a mortar. Note whether formaldehyde is liberated during the heating, as well as the effect of the addition agent on the cure. Remove the film from the hot plate and test its resistance to water by immersing it in a container of water.

Sample	*Result of Cure*	*Water Resistance of Film*
Dimethylolurea	....	....
Dimethylolurea plus ethylenediamine	....	....
Dimethylolurea plus hexamethylenetetramine	....	....
Dimethylolurea plus sodium chloroacetate or chloroacetamide	....	....
Dimethylolurea plus oxalic acid or phthalic anhydride	....	....

Preparation and Resinification of Sesquimethylolurea

Prepare a sample of sesquimethylolurea having an average of 1.5 moles of formaldehyde per mole of urea by blending (*a*) three parts of monomethylolurea with four parts of dimethylolurea, or (*b*) one part of urea with six parts of dimethylolurea. Heat a small sample of this mixture alone as a control. Also heat additional portions with a very small amount (about 1%) of each of the following indicated substances, previously blended together by grinding in a mortar. Note whether formaldehyde is liberated, also the effect of the addition agent on the cure. Test the water resistance of the films by submersion in water.

Sample	*Result of Cure*	*Water Resistance of Film*
Sesquimethylolurea	....	....
Sesquimethylolurea plus ethylenediamine	....	....
Sesquimethylolurea plus hexamethylenetetramine	....	....
Sesquimethylolurea plus sodium chloroacetate or chloroacetamide	....	....
Sesquimethylolurea plus oxalic acid	....	....

Acid Catalysis of Urea-Formaldehyde Resinification

A. Add 6 grams of urea to 15 grams of formalin and stir the mixture until solution of the urea occurs. Set aside for observation at the end of 5, 10, 15, 30, 60 minutes, and 24 hours.

B. Add 6 grams of urea to 15 grams of formalin, stir until solution of the urea is effected, and then add one drop of concentrated hydrochloric acid. Set aside for observation as in sample *A*.

QUESTIONS

1. Do the urea resins cure best under acid or alkaline conditions? How do they compare with the phenolic resins in this respect?
2. Compare the resinification of monomethylolureas and dimethylolureas.

3. Give a synthesis for each of the following:
    - *a.* Urea
    - *b.* Monophenylurea
    - *c.* Symmetrical dimethylurea
    - *d.* Unsymmetrical dimethylurea
    - *e.* Phenyldiethylurea
    - *f.* Tetrapropylurea

   Indicate which of the above ureas, if any, will not resinify when reacted with formaldehyde. Why?
4. Write the reaction for the preparation of monomethylolurea and dimethylolurea.
5. Why is an alkaline catalyst preferred to an acid catalyst for the initial condensation of urea and formaldehyde? Why does the apparently uncatalyzed reaction of urea and formalin behave as an acid-catalyzed reaction?
6. Would asbestos be a suitable filler for urea resins? How does this compare to the phenol-aldehyde resins?
7. Contrast the resinification and curing of the mono-, sesqui-, and dimethylolureas under neutral, alkaline, and acid conditions. Why does sodium chloroacetate behave as an acid? How does it differ from chloroacetamide?
8. Write the reaction for the etherization of mono- and dimethylolureas with butyl alcohol and ethylene glycol respectively.
9. Write the structure for a fully condensed urea-formaldehyde resin, and indicate the maximum mole ratio of formaldehyde to urea that can be retained in a fully cured resin.

Suggested Extensions

1. Prepare the methylol derivatives of a monoalkyl- or monoarylurea and compare with dimethylolurea.
2. Prepare the methylol derivatives of a symmetrical dialkyl- or diarylurea and compare with the products of Extension 1.
3. Prepare the methylol derivatives of an unsymmetrical dialkyl or diaryl derivative and compare with the products of Extensions 1 and 2.
4. Determine the residual formaldehyde in a urea reaction, using the hydroxylamine hydrochloride method (Test Method 1), and compare with the results obtained by the sulfite method (Test Method 2). Why is the sulfite method used?

EXPERIMENT 23

PREPARATION OF A UREA-FORMALDEHYDE MOLDING RESIN SYRUP

Part A. Preparation of Syrup

In a 1-liter round-bottomed flask fitted with a mechanical stirrer, thermometer, and reflux condenser place 260 grams of formalin. To this solution add 0.4 gram of sodium carbonate monohydrate, dissolved in a minimum amount of water and 10 grams of concentrated ammonium hydroxide. Mix the reactants with stirring and sample for formaldehyde content, using Test Method 2. This sample is labeled 00. Next add 120 grams of urea, stir the mixture until the urea dissolves, and sample for formaldehyde content. This sample is labeled 0. Heat the reaction in a suitable bath at 100 to 105° C. At the start of reflux, which is approximately 15 minutes after heat is applied, sample again for formaldehyde. This sample is labeled "reflux." Allow the reaction to proceed for 2 hours at a temperature at which the reaction refluxes very slowly. Sample for formaldehyde as indicated in the table below. Record the data in the following tabular form:

Sample	*Cubic Centimeters of Na_2SO_3 Solution*	*Grams of CH_2O per 100 cc*
00	....	....
0	....	....
Reflux	....	....
15 minutes after reflux	....	....
30 minutes after reflux	....	....
1 hour after reflux	....	....
2 hours after reflux	....	....

At the end of the 2-hour reaction period, cool immediately to room temperature. Determine the *p*H of the solution. If the *p*H is not between 6.8 and 6.5, adjust it to within these limits, either with citric acid or sodium carbonate solution as required. Weigh, bottle, and label the product. Determine the resin content and stroke cure of this syrup. This condensation product is to be used in Experiment 26.

Part B. Effect of *p*H on the Stability of the Condensation

To five 10-cc samples of the above condensation product, add 10% monochloroacetic or hydrochloric acid aqueous solution in the following volumes: 0.1 cc, 0.2 cc, 0.4 cc, 0.6 cc, 1.0 cc, 2.0 cc. Determine the *p*H of each sample after the addition. Observe the samples at the end of 2 hours and of 24 hours, and record the data.

			Observation	
Sample	*Amount of Acid*	*pH*	*2 Hours*	*24 Hours*
0	0.0 cc	....	....	....
1	0.1 cc	....	....	....
2	0.2 cc	....	....	....
3	0.4 cc	....	....	....
4	0.6 cc	....	....	....
5	1.0 cc	....	....	....
6	2.0 cc	....	....	....

Part C. The Effect of the *p*H and the Type of Curing Accelerator

To individual 10-cc samples add the quantity of reagent listed below. Determine the *p*H and the stroke cure of each sample at 130° C on the hot plate.

Group	*Sample*	*Addition*	*pH*	*Stroke Cure Time*
1	*a*	1 cc 1% citric acid aqueous solution	....	....
	b	1 cc 5% citric acid aqueous solution	....	....
	c	1 cc 10% citric acid aqueous solution	....	....
2	*d*	1 cc 1% hydrochloric acid aqueous solution	....	....
	e	1 cc 1% oxalic acid aqueous solution	....	....
	f	1 cc 10% sodium acid phthalate aqueous solution	....	....
3	*g*	1 cc 10% sodium chloroacetate aqueous solution	....	....
	h	1 cc 10% chloroacetamide aqueous solution	....	....

QUESTIONS

1. Explain the effect of *p*H on the stability of the syrup, and compare this to the original syrup. Explain the effect of the *p*H and the type of acid on the stroke cure.
2. Compare groups 1 and 2 relative to the ionization constants of the components of the groups. Which of the groups 1, 2, and 3 are direct accelerators? Which are latent accelerators? Which class is more desirable from a time-stability factor?
3. Distinguish between sodium chloroacetate and chloroacetamide. Which reacts with the urea-aldehyde condensation product?
4. Write the equation for the reaction between mono- and dimethylolurea and chloroacetamide.
5. Explain, how with chloroacetamide as part of the resin molecule, the polymer may be called a "self-curing" aminoplast.

Suggested Extensions

1. Study the resinification of thiourea with formaldehyde.
2. Study the resinification of urea with acetaldehyde and compare with the formaldehyde reaction product.

EXPERIMENT 24

PREPARATION OF A UREA-THIOUREA-FORMALDEHYDE MOLDING RESIN SYRUP

Part A. Preparation from Urea, Thiourea, and Formaldehyde

In a 1-liter round-bottomed flask fitted with mechanical stirrer, thermometer, and reflux condenser place 130 grams of formalin. To the formalin add 0.5 gram of sodium hydroxide in 5 cc of water, and then 4 grams of concentrated ammonium hydroxide. Because of the volatility of ammonia, a microburette is desirable for measuring the quantity required. An equivalent amount of hexamethylenetetramine may be used instead of the ammonia. Mix the reactants by stirring. Add to the reaction a mixture of 48 grams of urea and 15 grams of thiourea. Mix the reactants thoroughly, and immerse the reaction flask in a suitable heating bath at 100 to 105° C. Allow the reaction to continue for 2 hours after reflux starts. At the end of this period, cool, and, after testing, bottle and label the product which is to be used in preparing a molding powder in Experiment 26.

Part B. Preparation from Dimethylolurea, Thiourea, and Formaldehyde

In the same equipment as used above for the preparation of Resin *A*, mix the following reactants in the order stated.

1. Water	90	cc
2. Formalin	25	grams
3. NaOH in 5 cc of water	0.5	gram
4. Concentrated ammonium hydroxide	4	grams
5. Dimethylolurea	96	grams
6. Thiourea	15	grams

Reflux the ingredients for one hour. At the end of this period, cool to room temperature, and, after testing and comparing with Resin *A*, label and store for Experiment 26.

Tests on Product	*Resin A*	*Resin B*
1. Resin content	....	....
2. Weight of varnish	....	....
3. Viscosity	....	....
4. Precipitability	....	....
5. Stroke cure	....	....
6. Final *p*H	....	....

QUESTIONS

1. Explain any differences noted between a thiourea modified condensation and the unmodified urea-formaldehyde condensation.
2. Starting with inorganic materials only, give the equations for the synthesis of thiourea.

3. Give the formula for ammonium thiocarbamate.
4. Write the equations for the syntheses of (*a*) phenylthiourea, (*b*) symmetrical diphenylthiourea, (*c*) asymmetrical diphenylthiourea, (*d*) triphenylthiourea, and (*e*) tetraphylthiourea.
5. What are the advantages of a thiourea-modified urea resin? Its disadvantages?

Suggested Extension

1. Prepare a series of resins based on a series of mole ratios of urea to thiourea.

EXPERIMENT 25

PREPARATION OF UREA-MELAMINE-FORMALDEHYDE MOLDING RESIN SYRUPS

Using the procedure outlined in Experiment 24, react for one hour at reflux the ingredients indicated below. Add the ingredients in the order indicated and, after reflux, cool the samples, perform the required tests, bottle, label, and store for use in Experiment 26.

Part A. Preparation from Urea, Melamine, and Formaldehyde

Ingredients

1. Formalin	130 grams
2. NaOH in 5 cc of water	0.5 gram
3. Concentrated ammonium hydroxide	4 grams
4. Melamine	16 grams
5. Urea	48 grams

Part B. Preparation from Urea, Methylolmelamines, and Formaldehyde

Ingredients

1. Formalin	100 grams
2. NaOH in 5 cc of water	0.5 gram
3. Concentrated ammonium hydroxide	4 grams
4. Distilled water	20 grams
5. Methylolmelamines	27.5 grams
6. Urea	48 grams

Part C. Preparation from Dimethylolurea and Melamine

Ingredients

1. Distilled water	87 grams
2. NaOH in 5 cc of water	0.5 gram
3. Concentrated ammonium hydroxide	4 grams
4. Dimethylolurea	96 grams
5. Melamine	16 grams

Part D. Preparation from Dimethylolurea and Methylolmelamines

Ingredients

1. Distilled water	87 grams
2. NaOH in 5 cc of water	0.5 gram
3. Concentrated ammonium hydroxide	4 grams
4. Methylolmelamines	27.5 grams
5. Dimethylolurea	96 grams

Compare the four resin syrups for the following properties.

	Resin Syrup			
Tests	*A*	*B*	*C*	*D*
Clarity	....	....	....	....
Resin content	....	....	....	....
Weight of resin syrup	....	....	....	....
Viscosity	....	....	....	....
Stroke cure	....	....	....	....
Precipitability	....	....	....	....

QUESTIONS

1. Explain any differences noted between the melamine-modified urea-formaldehyde reactions and the urea-formaldehyde condensation. What advantages are gained by the melamine modification?
2. Give the chemical name for melamine and write its tautomeric formulas.
3. Give the synthesis of melamine, starting with (*a*) calcium cyanamide, (*b*) guanidine, (*c*) dicyandiamide, (*d*) biguanidine.
4. Write the equation for the reaction between melamine and (*a*) three moles of formaldehyde, (*b*) six moles of formaldehyde. Which is the stable methylol derivative with respect to formaldehyde retention?
5. How is 2,4,6-triaminopyrimidine related to melamine? How is it synthesized?
6. What are ammeline and thioammeline, and how are they prepared? How would you prepare thioammeline ethyl ether? Would it make a good resin?

Suggested Extensions

1. Prepare an unmodified melamine-formaldehyde resin.
2. Prepare a series of urea-melamine-formaldehyde resins, varying the ratio of urea to melamine. Compare the properties of the resins.
3. Prepare crystalline trimethylolmelamine, and study its resinification at different *p*H values.

EXPERIMENT 26

PREPARATION OF MOLDING POWDERS OF THE UREA AND MELAMINE TYPE

The preparation of a molding powder of this type consists of impregnating a filler with a resin in a liquid or solution form, removing a certain minimum amount of water and other volatile materials from the impregnated mass, reducing the dried material to a fine form for uniformity, and densifying the ground material if a mill or Banbury is available. Since the following powders are to be compared in the form of molded articles, the percentages of resin, fillers, procedures, etc., in each molding compound must be standardized. The compounding formula is as follows:

Resin on dry basis	55 parts
Filler	45 parts

Filler

Blend together thoroughly the following ingredients for at least 15 minutes, using a dough mixer or ball mill or tumbling barrel.

Alpha flock—200-mesh	44 parts
Lithopone—chloride free	0.5 part
Zinc stearate	0.5 part

Resin

From the known resin content of the syrup, calculate the weight of syrup required to equal 55 parts of solid resin.

$$\text{Weight of varnish required} = \frac{55 \times 100}{\%\ \text{Resin content}}$$

Add slowly the resin solution to the fillers and mix for at least 30 minutes if mechanical equipment such as a dough mixer is available. Otherwise, mix the ingredients manually in a beaker or aluminum pan, and continue mixing until all lumps are broken up. After it is mixed, spread the mixture on a watch glass or aluminum pan to dry in an air-circulating oven at 70 to 75° C until the material, when cooled to room temperature, can be ground. The approximate drying time is between 3.5 and 4.5 hours. If equipment is available for moisture determination, the water content of the powder should be reduced to less than 3% (Test Method 27). When the compound is dry, ball-mill the sample for 3 to 4 hours, or grind to a uniform powder in a mortar or a mechanical grinder.

Prepare at least one molding powder from each group listed below, especially those marked with an asterisk. If time permits, prepare all the powders in each group.

Group	*Varnish Syrup*	*Weight Syrup*	*% Resin*	*% H_2O in Dried Powder*
1	Exp. 23*A* *	....	....	....
2	Exp. 24*A* *	....	....	....
	24*B*	....	....	....
3	Exp. 25*A* *	....	....	....
	25*B*	....	....	....
	25*C*	....	....	....
	25*D*	....	....	....

Divide each of the ball-milled or ground samples into two equal parts. To one part add 0.3% by weight of phthalic anhydride or 0.5% by weight of chloroacetamide, and ball-mill again for one hour. Label the samples containing the phthalic anhydride or chloroacetamide as containing the accelerator with the letter *P*, and store all samples in water-tight containers.

These molding powders are to be used in Experiment 27. If milling rolls or a Banbury is available, the powders may be densified by processing for about 30 seconds at 110 to 120° C and regrinding the powder to a suitable size.

EXPERIMENT 27

PREPARATION OF UREA AND MELAMINE MOLDED ARTICLES

The molding powders of Experiment 26 are used in the preparation of these molded articles. Consult Experiment 16 on the molding of phenolic powders before proceeding with this experiment.

Heat the press platens and the mold to 135° C before charging the mold with the proper amount of molding powder. Use a pressure of 3000 pounds per square inch and apply for 5 minutes, maintaining the temperature at 135° C. At the end of 5 minutes release the pressure and remove the formed piece from the mold, without cooling the mold. Refer to the table below and prepare at least two molded samples from each of the molding compounds that are marked with an asterisk. If time permits, mold and test all samples. Those with the letter _P_ contain accelerators. Determine water resistance (Test Method 14) on all samples and record their appearance after boiling. Using a sharp-pointed instrument, determine qualitatively the surface hardness of the molded pieces, using 10 as the maximum value of hardness and 0 as lowest.

Test on Molded Samples

Sample	_Resin Type_	_Powder_	_Appearance of Molded Piece_	_% Water Absorption After Cycle_					_Appearance After Boiling_	_Surface Hardness_
				1	2	3	4	5		
1	Urea	23_A_ *	......	....	....	....	....	....	......	......
2	Urea	23_AP_ *	......	....	....	....	....	....	......	......
3	Urea-thiourea	24_A_ *	......	....	....	....	....	....	......	......
4	Urea-thiourea	24_AP_ *	......	....	....	....	....	....	......	......
5	Urea-thiourea	24_B_	......	....	....	....	....	....	......	......
6	Urea-thiourea	24_BP_	......	....	....	....	....	....	......	......
7	Urea-melamine	25_A_ *	......	....	....	....	....	....	......	......
8	Urea-melamine	25_AP_ *	......	....	....	....	....	....	......	......
9	Urea-melamine	25_B_	......	....	....	....	....	....	......	......
10	Urea-melamine	25_BP_	......	....	....	....	....	....	......	......
11	Urea-melamine	25_C_	......	....	....	....	....	....	......	......
12	Urea-melamine	25_CP_	......	....	....	....	....	....	......	......
13	Urea-melamine	25_D_	......	....	....	....	....	....	......	......
14	Urea-melamine	25_DP_	......	....	....	....	....	....	......	......

Light Stability

Compare the light stability of molded samples of urea, urea-thiourea, and urea-melamine molded pieces to each other and to a phenolic molded article by exposing each to sunlight or ultraviolet light for periods of 1, 2, and 3 weeks.

QUESTIONS

1. Explain the differences noted in the above molding powders, with particular reference to composition, formulation, curing properties, etc.
2. Explain the advantages and disadvantages of each of the compounds.
3. Since asbestos is either alkaline or tends to become alkaline, would it be logical to use asbestos as a filler in urea resins?

EXPERIMENT 28

PREPARATION OF UREA AND MODIFIED UREA LAMINATING RESIN SYRUPS

Part A. Preparation from Urea and Formaldehyde

In a round-bottomed, three-necked, 1-liter flask fitted with a reflux condenser, stirrer, and thermometer, mix the following ingredients in the order stated.

Formalin	190	grams
Sodium hydroxide in 6 cc of water	0.6	gram
Concentrated ammonium hydroxide	4	grams
Urea	60	grams

Immerse the reaction flask in a suitable bath heated to 110 to 120° C, bring the reaction to reflux, and react the mixture for 2 hours at reflux. Cool the reaction product to room temperature, and measure the *p*H of the resin solution. If the *p*H is not 7.3 to 7.5, adjust to within these limits with either 10% acetic acid or 10% sodium carbonate solution as required. Remove 50 to 55 cc of water from the resin solution by distillation under reduced pressure and at temperatures lower than 50° C. Cool to room temperature and add 2.5 grams of either sodium chloroacetate or chloroacetamide dissolved in a minimum amount of water. Filter the solution by suction, bottle, label, and store for Experiment 29.

Part B. Preparation from Dimethylolurea

In the same type of equipment as used in Part *A* of this experiment, introduce the following ingredients in the order stated and react for 2 hours at reflux temperature.

Dimethylolurea (dry basis)	120	grams
Distilled water	100	grams
NaOH in 6 cc of water	0.6	gram
Concentrated ammonium hydroxide	4	grams

At the end of the reflux time, cool to room temperature, and add 2.5 grams of either sodium chloroacetate or chloroacetamide dissolved in a minimum amount of water. Filter the resin solution by suction and, after testing, bottle, label, and store for use in Experiment 29.

Part C. Melamine Modified Urea-Formaldehyde Syrups

Using the procedure of Part *A* of this experiment, mix the following reactants in the order stated and react at reflux for 2 hours.

Formalin	190	grams
Sodium hydroxide in 6 cc of water	0.6	gram
Concentrated ammonium hydroxide	4	grams
Urea	50	grams
Melamine	20	grams

After reflux, cool to room temperature, adjusting the *p*H to 7.3 to 7.5 if necessary. Remove 50 to 55 cc of water by distillation at reduced pressures and at temperatures below 50° C. Cool the syrup to room temperature and add 2.5 grams of sodium chloroacetate or chloroacetamide dissolved in a minimum amount of water. Filter the solution by suction and store for Experiment 29.

Perform comparative tests on the three solutions and record the data.

Tests	*Method*	*Resin A*	*Resin B*	*Resin C*
1. Resin content, %	3	....	....	....
2. Weight of varnish		....	....	....
3. Viscosity	7	....	....	....
4. Stroke cure	4	....	....	....
5. Precipitability	9	....	....	....
6. *p*H—Final		....	....	....

The determination of the resin content of urea solutions is performed at 110° C as contrasted to 150° C for phenolic resin solutions. Urea resins break down at the higher temperature.

EXPERIMENT 29

PREPARATION OF A UREA-FORMALDEHYDE LAMINATING STOCK

Before starting this experiment review the procedure on laminating stock described in Experiment 11. The basic water-white color and light stability of urea-type resins permit the preparation of translucent and opaque panels in permanent pastel shades. The water resistance of urea panels is not too satisfactory, but it is considerably improved by modifying the urea condensation product by thiourea and melamine. For comparative purposes, at least two panels are to be prepared, one set from an unmodified and the other set from a modified urea resin.

Translucent Panels

The translucent panels are prepared from an especially high-quality, uniformly highly absorbent rag stock paper (paper *A*). To achieve sufficient and uniform translucency, a resin content of at about 60% is required. More than 65% resin produces brittle products. However, paper impregnated with as much as 70% resin may be used as face sheets on cores containing a very low percentage of resin. The volatile content of translucent sheet stock prior to laminating must be between 6 and 8%.

White Opaque Panels

A high-quality non-yellowing rag stock paper (paper *B*) containing a stable white pigment is used for the preparation of the treated stock. The pigmentation in the paper must be uniform and evenly dispersed. A resin content of 48 to 55% and a volatile content of 4 to 5% in the impregnated sheet stock before laminating is satisfactory in the treated sheet stock.

Impregnated Sheets

The paper to be treated is cut into sheets 7 by 13 inches long so that, after drying, they can be recut to 6 by 6 inches for future pressing operations. If one dip does not deposit sufficient resin, dry the first dip for only 10 minutes at 110° C. If a second or third dip is necessary, dry that dip for about 5 minutes; but, in any case, dry the last dip at 110° C to the proper volatile content, using one especially marked sheet as a "control sheet." Dip ten sheets of each paper in each of the two varnishes and record the data in the following table, using the indicated resin solutions.

			Translucent Stock Using Paper A			
Sheet Stock	*Resin Solution to Be Used*	*Dip*	*Weight of Paper*	*Weight of Treated Paper*	*% Resin*	*% Volatile*
29*A*	Urea resin of Exp. 28*A* or 28*B*	Single	....	....	....	....
		Double	....	....	....	....
		Triple	....	....	....	....
29*B*	Urea-melamine resin of Exp. 28*C*	Single	....	....	....	....
		Double	....	....	....	....
		Triple	....	....	....	....
			Opaque Stock Using Paper B			
29*C*	Urea resin of Exp. 28*A* or 28*B*	Single	....	....	....	....
		Double	....	....	....	....
		Triple	....	....	....	....
29*D*	Urea-melamine resin of Exp. 28*C*	Single	....	....	....	....
		Double	....	....	....	....
		Triple	....	....	....	....

The laminated stock is stored in a sealed container to prevent moisture pick-up if it is not used within one hour of its drying to the proper volatile content.

EXPERIMENT 30

PREPARATION OF A UREA-FORMALDEHYDE LAMINATED PANEL

Cut the 13 by 7 inch treated stock of Experiment 29 to 6 by 6 inch panels. In trimming, remove those edges that show an accumulation of excess resin as a result of dripping and draining during the impregnation process. Stack ten sheets each of the 6 by 6 inch panels and press at 125 to 130° C for 45 minutes. Cool the panels to room temperature before removal from the press. Trim the edges of the cured panels and observe their translucency or opacity. Cut 1 to 6 inch strips from the sheet for water absorption and for boiling water resistance. Compare the resistance of the urea panel to the urea-melamine panel. Record the data in the chart below, noting particularly the time required to produce failure in boiling water.

Panel	*Sheet Stock*	*% Water Absorption—24 Hours*	*Appearance After Boiling Water*			*Time of Failure*	*Type of Failure*
			15 Min.	*1 Hr.*	*Time of Failure*		
1	29*A*	....	....	....	....	....	....
2	29*B*	....	....	....	....	....	....
3	29*C*	....	....	....	....	....	....
4	29*D*	....	....	....	....	....	....

EXPERIMENT 31

PREPARATION OF A UREA-FORMALDEHYDE BUTYL ALCOHOL RESIN FOR VARNISHES

In a 1-liter, three-necked, round-bottomed flask, fitted with stirrer, reflux condenser, and thermometer, and heated by a suitable bath, place 150 grams of formalin and 260 grams of butyl alcohol. To the solution add 30 grams of urea, and stir the mixture until the urea dissolves. Heat the reaction on the bath at 100 to 110° C until it refluxes, and react one hour at reflux. Cool, and determine the *p*H. Determine the resin content by heating for 90 minutes at 110° C. A higher temperature is avoided lest a breakdown of the butylated resin occur. Record the following data:

Initial *p*H	....	Weight of material	....
Adjusted *p*H	....	Amount of resin	....
Resin content	....	Resin per mole of urea	....

Dehydrate the resin mixture by converting the apparatus to a Stark and Dean dehydrating equipment as in Figure 6. Fill the trap with toluene before starting the dehydration. Use a 25-cc Stark and Dean trap with a stopcock built into the receiving well so that the water may be drained off as it is collected during reflux. Collect the water layer (which also contains dissolved butanol, etc.) until no more water of reaction is eliminated (about 65 cc). Cool the reaction mass to room temperature and suction-filter the varnish solution. Using a clean reaction flask, return the filtered varnish to the Stark and Dean apparatus and remove 50 cc more of butyl alcohol. Cool the solution and dilute with 80 cc of toluene. Determine the resin content, weight of material, and record the following data:

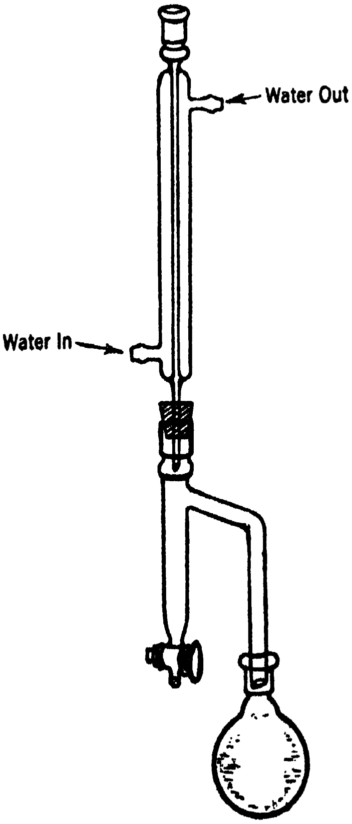
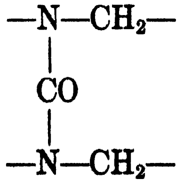


FIGURE 6. Continuous Dehydration Apparatus.

Weight of material	....	Amount of resin	....
Resin content	....	Resin per mole of urea	....

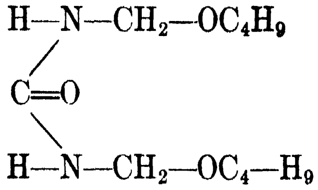
Bottle, label the sample, and store for use in Experiment 37.

On the assumption that 1 mole or 60 grams of urea, when completely reacted with formaldehyde and completely cured, contains the repeating unit



$$\begin{array}{c} -N-CH_2- \\ | \\ CO \\ | \\ -N-CH_2- \end{array}$$

or 84 grams of resin, and that urea, formaldehyde, and butyl alcohol react to give the butyl ether of dimethylolurea,



or 232 grams, calculate the extent to which the resin prepared was butylated, using the formula

$$(84x) + (1 - x)(232) = \frac{(\text{Wt. of resin obtained})(60)}{(\text{Wt. of urea used})}$$

where x represents the fraction of urea converted to an unmodified resin and $(1 - x)$ is the fraction of butylated resin.

Study the solubility of the butylated resin in the following solvents.

Solvent	*Solubility*
Water	....
Ethyl alcohol	....
Ethylene glycol	....
Ether	....
Benzene	....
Petroleum ether	....
Butyl acetate	....

QUESTION

1. Explain the solubility results, and compare these to an ordinary urea-formaldehyde condensation product.

Suggested Extensions

1. Prepare a urea-formaldehyde, alcohol-modified resin, starting with dimethylolurea, water, and butyl alcohol. Compare this product with the preparation of this experiment.
2. Recover quantitatively the water and butyl alcohol from the above experiment, and compare these values with the original materials used and with the resin obtained.
3. Starting with methyl alcohol, prepare a series of alcohol-modified urea resins up to and including hexyl alcohol. Test these modified resins for solubility in hydrocarbon solvents.
4. Study the modifications of the urea-formaldehyde reaction by the polyhydric alcohols, such as ethylene glycol, diethylene glycol, and glycerol.

EXPERIMENT 32

PREPARATION OF A MELAMINE-FORMALDEHYDE BUTYL ALCOHOL RESIN FOR VARNISHES

In a 1-liter, three-necked flask, fitted with thermometer, reflux condenser, and mechanical stirrer, and heated in a suitable bath, react 60 grams of melamine, 160 grams of formalin, and 220 grams of butyl alcohol at reflux for 30 minutes.

Dehydrate the material by using a Stark and Dean apparatus (Figure 6), having first filled the dehydration trap with benzene or toluene. Draw off water from the dehydration trap until no more is collected. Then draw off 20 to 25 cc of butyl alcohol. Allow the varnish to cool, and determine the resin content of the remainder. Dilute with anhydrous butyl alcohol to a 50% resin content. Filter the solution, bottle, label, and store for use in Experiment 37.

Determine the solubility of the varnish in the following solvents.

Solvent	*Solubility*
Alcohol	....
Ether	....
Benzene	....
Petroleum ether	....
Ethylene glycol	....
Butyl acetate	....

Suggested Extensions

1. Prepare a series of butylated urea-melamine-formaldehyde resins.
2. Modify the resin with other aldehydes, such as acetaldehyde, acrolein, and furfuraldehyde.

EXPERIMENT 33

RELATIONSHIP OF ALKYD RESINS TO THE STRUCTURE OF REACTANTS

Prepare the alkyd resins indicated below in open 250-cc beakers on electric hot plates, the surface temperatures of which are 250 to 300° C. Stir the reactions slowly with mechanical stirrers. Sample the reactions at the indicated intervals. Determine the acid number (Test Method 19) and solubilities as directed. At each sampling, spot out a drop or two of material on a glass plate and observe the type of resin as to viscosity, hardness, stringiness, etc. Determine and record the gelation time at 280° C.

Alkyd Resin A

React one-half mole of phthalic anhydride with one-third mole of glycerol. Calculate and record the acid number of the original mixture. As the reaction proceeds, the resinous material becomes brittle when cooled. Pour into a cooling pan, break up for future use, bottle, and label. Determine the solubility of each sample in 50 : 50 toluene-butyl acetate mixture (solvent *A*) and in 75 : 25 toluene-butyl acetate mixture (solvent *B*), and record, together with other data, in the following table:

Sample	*Temperature*	*Acid Number*	*Gelation Time at 280° C*	*Description of Resin*	*Solubility*	
					Solvent A	*Solvent B*
At melt	....	....	....	....	....	....
5-minute	....	....	....	....	....	....
10-minute	....	....	....	....	....	....
15-minute	....	....	....	....	....	....
30-minute	....	....	....	....	....	....
45-minute	....	....	....	....	....	....
Final	Approx. 230° C	....	....	....	....	....

Alkyd Resin B

React one-half mole of redistilled ethylene glycol and one-half mole of phthalic or succinic anhydride. Calculate the acid number for the original mixture ________. Record the necessary data as in alkyd resin *A*.

Sample	*Temperature*	*Acid Number*	*Gelation Time at 280° C*	*Description of Resin*	*Solubility*	
					Solvent A	*Solvent B*
At melt	....	....	....	....	....	....
10-minute	....	....	....	....	....	....
15-minute	....	....	....	....	....	....
30-minute	....	....	....	....	....	....
45-minute	....	....	....	....	....	....
Final	Approx. 235° C	....	....	....	....	....

Alkyd Resin C

React one-half mole of diethylene glycol and one-half mole of maleic anhydride. Calculate the acid number for the original mixture ________. Record the necessary data as in alkyd resin *A*.

Sample	*Temperature*	*Acid Number*	*Gelation Time at 280° C*	*Description of Resin*	*Solubility* *Solvent A*	 *Solvent B*
At melt	....	....	....	....	....	....
10-minute	....	....	....	....	....	....
15-minute	....	....	....	....	....	....
30-minute	....	....	....	....	....	....
45-minute	....	....	....	....	....	....
Final	Approx. 235° C	....	....	....	....	....

QUESTIONS

1. What phenomenon did you observe in resin *C*? To what chemical reaction is it due? How could it be prevented?
2. Explain the differences between resin *A* and resin *C*. Is the gelation of resin *A* and resin *C* due to the same type of chemical reaction?
3. Does alkyd resin *B* gel and why? Explain the gelation or heat convertibility of the three resins.
4. Explain the changes in solubility in each resin as the reaction proceeds.
5. What is the natural source of glycerol? How is it made synthetically?
6. Describe the commercial syntheses of phthalic anhydride and of maleic anhydride. How would you prepare phthalic anhydride in the laboratory?

EXPERIMENT 34

COMPARISON OF ALKYD RESINS MODIFIED WITH FATTY ACID

Part I. The Preparation of Modified Alkyd Resins

React the materials indicated below in an open beaker on a hot plate, preferably the same plate and temperature as in Experiment 33. Stir the reaction slowly with a mechanical stirrer throughout the experiment. It is suggested that, after the temperature reaches 130° C, it should be raised at the rate of 1° C per minute until a temperature of 235° C is reached, and then held at that temperature for 15 minutes. Sample at the indicated intervals, and determine the solubility in solvent *A* (50 : 50 toluene-butyl acetate mixture), and in solvent *B* (75 : 25 toluene-butyl acetate mixture) as in Experiment 33. Describe the resin as the reaction proceeds. It may be done conveniently by spotting out a small sample on a cold glass plate and allowing the resin to come to room temperature. Note when the reactants become compatible as evidenced by a clear resin. Determine their gelation times at about 280° C, using Test Method 20, and record the data on the following charts.

Alkyd Resin A—Modified with Linseed Oil.

Phthalic anhydride	27 grams
Glycerol	15 grams
Linseed-oil fatty acids	26 grams

Sample	*Temperature*	*Solubility* *Solvent A*	*Solvent B*	*Gelation Time*	*Description of Resin, e.g., Cloudy, Clear, Hard*
At melt	....	....	....	....	....
5-minute	....	....	....	....	....
10-minute	....	....	....	....	....
20-minute	....	....	....	....	....
30-minute	... .	....	....	....	....
40-minute	....	....	....	....	....
Final	Approx. 235° C	....	....	....	....

Pour the resin into a cooling pan and save it for Part II of this experiment.

Alkyd Resin B—Modified with Tung Oil.

Phthalic anhydride	27 grams
Glycerol	15 grams
Tung-oil fatty acids	26 grams

Sample	*Temperature*	*Solubility*		*Gelation Time*	*Description of Resin, e.g., Cloudy, Clear, Hard*
		Solvent A	*Solvent B*		
At melt	....	....	....	....	....
5-minute	....	....	....	....	....
10-minute	....	....	....	....	....
20-minute	....	....	....	....	....
30-minute	....	....	....	....	....
40-minute	....	....	....	....	....
Final	Approx. 235° C	....	....	....	....

Pour the resin into a cooling pan and save it for Part II of this experiment.

Alkyd Resin C—Modified with Castor Oil.

Phthalic anhydride	27 grams
Glycerol	15.5 grams
Castor-oil acids	26 grams

Sample	*Temperature*	*Solubility*		*Gelation Time*	*Description of Resin, e.g., Cloudy, Clear, Hard*
		Solvent A	*Solvent B*		
At melt	....	....	....	....	....
5-minute	....	....	....	....	....
10-minute	....	....	....	....	....
20-minute	....	....	....	....	....
30-minute	....	....	....	....	....
40-minute	....	....	....	....	....
Final	Approx. 235° C	....	....	....	....

Pour the resin into a cooling pan and save it for Part II of this experiment.

Compare the three resins by making the following observations on the 30-minute samples.

Resin	*Solubility*		*Flexibility*	*Hardness*	*Type of Resin*	*Brittleness*
	Solvent A	*Solvent B*				
A	....	....	....	....	....	....
B	....	....	....	....	....	....
C	....	....	....	....	....	....

Part II. The Air and Heat Convertibility of Modified Alkyd Resins

Prepare a 50% (by weight) solution of resins 34*A*, 34*B*, 34*C* in solvent *B* and use for the tests below. Store part of the 50% solutions of resins 34*A* and 34*B* for use in Experiment 37.

Test A. Baking Properties. Deposit films of each resin on glass plates by flowing a sample of the varnish over the glass and allowing it to drip vertically. Bake the three films in an oven at 150° C and record the following data. The type of film is recorded as flexible, tough, brittle, etc.

Resin	*Freedom from Tack*	*Oven Temperature Hard and Dry*	*Type of Film*	*Color*
34*A*	....	....	....	....
34*B*	....	....	....	....
34*C*	....	....	....	....

Test B. Air-Drying Properties. For this test *do not* add driers to your larger supply of solutions of the resins since they are to be used without driers in Experiment 37. Withdraw 50-cc samples of each of the resins, 34*A*, 34*B*, and 34*C*, and to each add 0.1 gram of naphthenate driers and prepare films by pouring on glass as in Test *A*. Air-dry these films at room temperature and report their condition in 3, 6, and 24 hours, i.e., whether they are tacky, dry, and soft, or dry and hard. Record the color and finish of the films after 48 hours of drying.

	Data					
Resin	*3 Hours*	*6 Hours*	*24 Hours*	*48 Hours*	*Color*	*Type of Film*
34*A*	....	....	....	....	....	....
34*B*	....	....	....	....	....	....
34*C*	....	....	....	....	....	....

QUESTIONS

1. Do the results of this experiment indicate that some alkyds are preferred for baking varnishes and others are best suited to drying varnishes? Explain your answer.
2. Does the nature of the unsaturated fatty acid change the drying rate?
3. List and write the structures of at least ten drying and semi-drying oils.
4. How may drying oils be made synthetically? What are they?

Suggested Extensions

1. Modify the alkyd resins with oil-soluble phenol alcohols and determine the increase in water, chemical, and solvent resistance.
2. Precondense glycerol and phthalic anhydride to a series of different acid numbers prior to condensation with a fatty acid. Due account must be taken of mole equivalents.
3. Precondense glycerol and a drying oil in the presence of a small amount of sodium carbonate until a clear solution results. Then react with phthalic anhydride.

EXPERIMENT 35

ESTER EXCHANGE PREPARATION OF ALKYD RESINS

Part A. Castor-Oil Ester Exchange

Following the general procedure of the previous experiments, react, with stirring, 15 grams of raw castor oil, 28 grams of glycerol, and 0.3 gram of sodium carbonate in an open 250-cc beaker at about 170 to 180° C until the reagents become compatible. This will require approximately 30 minutes. Next add 15 grams of castor-oil acids and 42 grams of phthalic anhydride. While stirring slowly, raise the temperature to 200° C, and maintain at that temperature for approximately 20 minutes, or until the reactants are compatible when cold. This may be determined by testing a drop on a cold glass plate. React the mixture for about 55 minutes, slowly raising the temperature to a maximum of about 240° C. Allow the resin to cool to about 130° C, and dilute with 100 cc of toluene in the absence of flames. Determine the resin content, bottle, and label for Experiment 37. Determine its gelation time.

Part B. Linseed-Oil Ester Exchange

React with stirring, and according to Part *A* of this experiment, 27 grams of linseed oil, 12.4 grams of glycerol, and 0.2 gram of sodium carbonate in an open 250-cc beaker at about 170 to 180° C until the reagents become compatible. Add next 26.9 grams of phthalic anhydride while slowly raising the temperature to a maximum of about 240° C. Allow the resin to cool to about 130° C and dilute with 100 cc of toluene. Determine the resin content, bottle, and label for Experiment 37. Determine its gelation time.

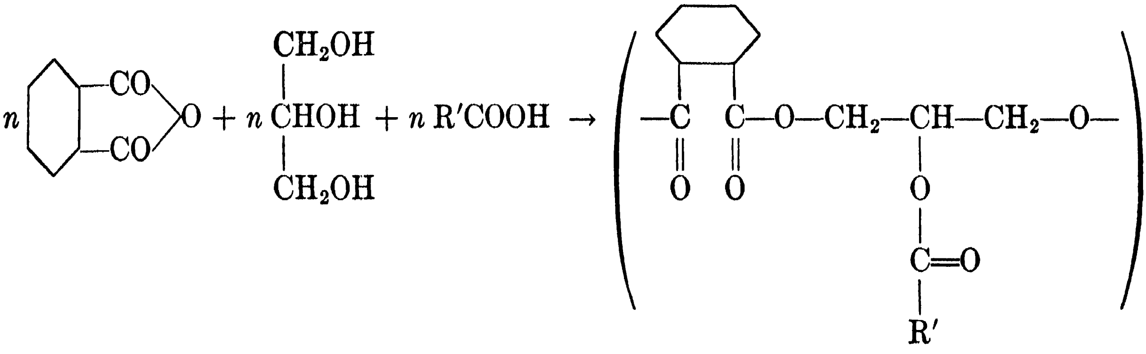
QUESTION

1. Does resin 35*A* air-dry? Explain your answer and contrast it with resin 35*B*.

EXPERIMENT 36

PREPARATION OF A SERIES OF ALKYD RESINS FOR COATINGS

The simplest drying-oil alkyd resin is prepared by reacting one mole of glycerol, one mole of phthalic anhydride, and one mole of a drying-oil fatty acid. The polymeric reaction product is represented structurally as follows.



A slight excess of glycerol is used since complete esterification of the three hydroxyl groups is not obtained. In the following table, formula *A* represents the fatty-acid monoglyceride phthalate resin. The other formula represents the same resin modified by increasing amounts of glycerol and phthalic anhydride in a ratio equivalent to glyceryl phthalate with a slight excess of glycerol. As more glyceryl phthalate is added to the basic resin molecule, the oil content is proportionately reduced as the phthalic anhydride content is proportionately increased. By class cooperation, this series of alkyd resins can be prepared and properties versus composition studied. Prepare these alkyds according to the principles already learned in previous experiments. Advance the resins to a 10 to 12 inch string before cutting to a 50% solids content with a solvent of 50% toluene and 50% butyl acetate. Add driers to the solution, prepare air-dried and baked films, etc., and summarize the data in a written report to your instructor, correlating the results with composition if possible.

Materials	*A*	*B*	*C*	*D*	*E*
Phthalic anhydride	148	148 + 37	148 + 74	148 + 111	148 + 148
Glycerol	100	100 + 16.5	100 + 33	100 + 49.5	100 + 66
Linseed fatty acids	261	261	261	261	261
% Linseed fatty acids	...	...	...	...	...
% Phthalic anhydride	...	...	...	...	...

QUESTION

1. Distinguish between a heat-convertible and an element-convertible alkyd resin.

EXPERIMENT 37

COMPATIBILITY OF ALKYD RESINS WITH BUTYLATED AMINOPLAST RESINS

Prepare the following compositions in the relative volumes of the solutions indicated below. Note the compatibility of the solutions and determine the stroke cure at 130° C. Pour films of the mixed solutions and bake for one hour at 150° C. Note the nature of the baked film for compatibility, color, hardness, and clarity. Test the resistance of the baked films to boiling water for 15 minutes.

Part A

Parts of Urea Resin of Exp. 31	*Parts of Alkyd Resin of Exp. 35A*	*Solution Compatibility*	*Solution Cure Time*	*Type of Stroke Cure*	*Baked Film*	*Water Resistance*
75	25	....	....	....	....	....
50	50	....	....	....	....	....
25	75	....	....	....	....	....

Part B

Melamine Resin of Exp. 32	*Alkyd Resin of Exp. 35A*					
75	25	....	....	....	....	....
50	50	....	....	....	....	....
25	75	....	....	....	....	....

Part C

50 Parts of Resin of Exp.:	*50 Parts of Resin of Exp.:*					
31	34*A*	....	....	....	....	....
31	34*B*	....	....	....	....	....
32	34*A*	....	....	....	....	....
32	34*B*	....	....	....	....	....

QUESTIONS

1. What general conclusion can be drawn as to the nature of the fatty acid component of the alkyd resin when compatibility with aminoplast resins is required?
2. Which gives the harder and more water-resistant film, the urea or the melamine modified resins?

EXPERIMENT 38

PREPARATION OF DIETHYLENE GLYCOL MALEATE

In a 125-cc distilling flask, set downward for distillation and fitted with thermometer and gas bubbling tube, both extending nearly to the bottom of the flask, place 53 grams of redistilled diethylene glycol and 44 grams of maleic anhydride. Bubble in deoxygenated nitrogen until the air in the flask is replaced by nitrogen. Commercial cylinder nitrogen can be deoxygenated by passing the gas over copper turnings heated to 300 to 350° C, or by bubbling through 10% pyrogallol, drying, etc. Heat the flask and reaction mixture to 210 to 220° C. This heating can be done carefully over a wire gauze. Hold the reaction at this temperature for 2 to 4 hours. Allow the mixture to cool with nitrogen still passing into the system. The result should be a light yellow, viscous, liquid, diethylene glycol maleate. Determine the acid number. Store in a wide-mouthed bottle for use in Experiments 39 and 40.

QUESTIONS

1. Explain the differences in this experiment and the results obtained in preparation of the alkyd resin *C* of Experiment 33.
2. Are maleic acid resins oxygen sensitive?
3. Give the syntheses of:

    1. Ethylene oxide
    2. Ethylene glycol
    3. Diethylene glycol
    4. Maleic anhydride

EXPERIMENT 39

POLYMERIZATION OF DIETHYLENE GLYCOL MALEATE

Part A. Air versus Benzoyl Peroxide Polymerization

Prepare a solution of 10 grams of diethylene glycol maleate in 20 cc of a 50 : 50 mixture of acetone and amyl acetate. Divide the solution into two parts. To one part add 0.05 gram of benzoyl peroxide. Make two films on glass from each solution. Dry one of the films at room temperature and the other in an oven at about 110° C. Record the time to produce films free of tack.

		Drying Time	
Film 1	Diethylene glycol maleate Solvent mixture	Air-dry .... ° C	Oven-dry .... ° C
Film 2	Diethylene glycol maleate Solvent mixture Benzoyl peroxide	....	....

Part B. Drying-Oil Type Polymerization

Prepare a solution of 10 grams of diethylene glycol maleate in 20 cc of a 50 : 50 mixture of acetone and amyl acetate. Divide into two parts. To one part add approximately 0.1% of a solution of naphthenate driers and to the other part approximately 0.5% of the same driers.

Make two films on glass from each part, drying one film at room temperature and the other in an oven at 110° C. Record the time required to produce a film free of tack.

		Drying Time	
Film 3	Diethylene glycol maleate Solvent mixture 0.1% driers	Air-dry .... ° C	Oven-dry .... ° C
Film 4	Diethylene glycol maleate Solvent mixture 0.5% driers	....	....

QUESTION

1. Indicate how cross-linking occurs in linear resins such as glycol maleate and diethylene glycol maleate. What is the analogy to rubber vulcanization?

EXPERIMENT 40

COPOLYMERS OF MALEIC ESTERS OF POLYHYDRIC ALCOHOLS

Part A. Cured Films

Prepare two films from the composition indicated below. Compare the time required to obtain tack-free films at room temperature and in an oven at 70 to 80° C.

Time to Dry

Air ....° C Oven ....° C

Diethylene glycol maleate	10.0 grams
Benzoyl peroxide	0.05 gram
Uninhibited styrene	2.0 grams
Butyl acetate	8.0 cc

Part B. Mass Castings

Prepare a mixture of (*a*) 20 grams of diethylene glycol maleate and (*b*) 10 grams of uninhibited styrene, in which 0.2 gram of benzoyl peroxide is dissolved. Mix well, and pour into 5-cc vials, using approximately 4 cc per vial. Treat the vials as follows:

Vial 1. Allow to remain at room temperature in the dark.
Vial 2. Allow to remain at room temperature in the sunlight.
Vial 3. Allow to remain at room temperature in sunlight until it becomes solid; then place in a 50° C oven.
Vial 4. Place in a 50° C oven.

Record the following data, and in the description of the product note the color, the formation of cracks, charring, etc.

	Time		
Casting	*Solid Gelation*	*Hard Solid*	*Description of Product*
Vial 1	....	....	....
Vial 2	....	....	....
Vial 3	....	....	....
Vial 4	....	....	....

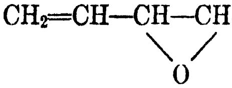
Part C. Low-Pressure Laminating

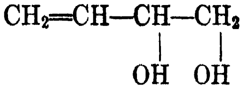
Mix together 20 grams of diethylene glycol maleate and 10 grams of uninhibited styrene in which is dissolved 0.5 gram of benzoyl peroxide. Stir the solution until it is uniform, and transfer to a flat dish or pan for impregnation of filter paper. Attach a clean paper clip to one end of a sheet of high-quality filter paper and, by holding on to the clip, immerse the paper in the resin solution for 45 to 60 seconds, or until the paper is thoroughly saturated. Remove the sheet from the solution and allow it to drain for about 5 minutes by suspending the impregnated sheet by means of the paper clip. Treat five filter sheets in this fashion and stack them between two sheets of glass previously dusted with zinc stearate on the surfaces contacting the resin. Place the glass plates containing the sandwich of impregnated sheets in an oven flatwise at 80° C. Calculate the surface area of the filter paper and on the top sheet of glass add enough weights to give 2 to 3 pounds of pressure per square inch of impregnated paper surface. Allow the sheets to cure for about 4 to 6 hours and, if still tacky or soft at that time, continue heating, raising the temperature to 100° C, until a hard product is obtained.

QUESTIONS

1. Contrast the results of this experiment with those of Experiment 39.
2. Write the equation showing how copolymerization of the styrene and the maleic ester is accomplished.
3. What is the function of the styrene?

Suggested Extensions

1. Undertake a series of studies, using varying proportions of styrene and diethylene glycol maleate.
2. Study the effect of peroxide concentration, particularly on the resulting exothermic reaction.
3. Use other organic compounds containing the $CH_2{=}C\langle$ grouping, e.g., vinyl acetate, the acrylic esters, the methacrylic ester, as well as monomers containing a multiplicity of $CH_2{=}C\langle$ groupings, e.g., diallyl phthalate, diallyl maleate, and diallyl ether.
4. Prepare an alkyd resin from either succinic or phthalic acid and butadiene monoxide and compare copolymers of this resin and $CH_2{=}C\langle$ compounds with the maleic alkyd resins of this experiment. The butadiene monoxide has the formula  $CH_2{=}CH{-}\underset{\diagdown\ O\ \diagup}{CH{-}CH_2}$, which corresponds to the epoxide of the dihydric alcohol



$$CH_2{=}CH{-}\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH_2}}$$

5. Prepare an alkyd resin from butadiene monoxide and an aliphatic unsaturated dibasic acid, e.g., maleic acid. Compare this alkyd to the alkyd of this experiment and to the alkyd of Suggested Extension 4.

EXPERIMENT 41

POLYMERIZATION OF STYRENE

Part A. Mass Casting

Make up six 20-cc samples of uninhibited, freshly vacuum-distilled styrene. Styrene may be safely distilled in the presence of small quantities of sulfur. Add benzoyl peroxide to the samples in the following concentrations.

Sample	*Percentage of Benzoyl Peroxide*
0	0.00
1	0.05
2	0.10
3	0.15
4	0.20
5	1.00

Polymerize the styrene samples by heating in a suitable oven or bath at 80° C. At the end of 24 and 144 hours, remove and titrate aliquot portions of each liquid sample for unsaturation, diluting with a solvent such as benzene or carbon tetrachloride if necessary (Test Method 21). Compare this titration with the value obtained for titrating a definite quantity of monomeric styrene. Calculate the average molecular weights of the different samples by using the method of Part *B* of this experiment.

Part B. Molecular Weight Determination

Calculation of Molecular Weight. Staudinger has proposed the following formula for the calculation of the molecular weight of the long-chain polymers from the viscosity of a dilute solution of the polymer in an appropriate solvent:

$$K_m M = \frac{\eta_{sp}}{C}$$

where M is the molecular weight of the long-chain polymer.

$$\eta_{sp} \text{ is the specific viscosity} = \left(\frac{\text{Time of efflux of polymer solution at } 20^\circ \text{ C}}{\text{Time of efflux of solvent at } 20^\circ \text{ C}}\right) - 1.$$

C is the concentration of polystyrene in the solvent, generally called fundamental molarity, which is based on the molecular weight of the molecule forming the unit of chain structure, i.e., the monomer, $C = 1$, when 104 grams of polystyrene is dissolved in 1000 ml of solvent at 20° C.

K_m is a characteristic constant for each polymer in a particular solvent. For polystyrene, $K = 1.8 \times 10^{-4}$ in benzene, toluene, or tetralin.

To satisfy the condition of a dilute solution, C should be about 0.01 molar, i.e., the concentration of polystyrene in solvent should be about 1 gram in 1000 ml of solvent at

20° C. The specific viscosity should be in the neighborhood of 0.3 for accurate results. Viscosity measurements are to be made with an Ostwald viscometer at 20° C, using whatever sections of Test Method 7 are required. The solution of the polymer should not be turbid as only a clear solution can be used for viscosity measurements. Filter the solution if necessary.

Calculations. A typical example to show what data must be obtained is this.

Sample Styrene Containing Benzoyl Peroxide Catalyst

Weight of sample = 0.0909 gram
Volume of solvent at 20° C = 67.5 ml

$$\text{Fundamental molarity} = \frac{0.0909}{67.5} \times \frac{1000}{104} = 0.0129$$

Time of efflux of polymer solution = 17.4 seconds
Time of efflux of solvent = 13.2 seconds

$$\text{Specific viscosity } \frac{(17.4)}{(13.2)} - 1 = 0.32$$

$$M = \frac{\eta_{sp}}{K_m C} = \frac{0.32}{(1.8 \times 10^{-4})(0.0129)} = 137{,}800+$$

Sources of Error

1. In weighing.
2. Variations in solvent volume in viscometer.
3. In viscosity measurements.
4. Deviations from Staudinger equation.
5. Miscellaneous.

With care the experimental errors can be kept low, and probably will not exceed 2%.

Record of Data

		Degree Unsaturation, cc Titrant Solution	*Weight*		*Time*		*Average Molecular Weight*
Monomer Sample			*Sample, 20° C*	*Solvent, 20° C*	*Efflux Solution, 20° C*	*Efflux Solvent, 20° C*	
Sample 0	24 hours	....	....	....	....	....	....
	144 hours	....	....	....	....	....	....
Sample 1	24 hours	....	....	....	....	....	....
	144 hours	....	....	....	....	....	....
Sample 2	24 hours	....	....	....	....	....	....
	144 hours	....	....	....	....	....	....
Sample 3	24 hours	....	....	....	....	....	....
	144 hours	....	....	....	....	....	....
Sample 4	24 hours	....	....	....	....	....	....
	144 hours	....	....	....	....	....	....
Sample 5	24 hours	....	....	....	....	....	....
	144 hours	....	....	....	....	....	....

A more accurate determination of molecular weight can be made by plotting the value of specific viscosity over concentration versus concentration and extrapolating to the intrinsic viscosity at zero concentration. This value is $[\eta]$, and the equation $K_m M^a = [\eta]$ is used for the calculation of molecular weight M. The exponent a has a value of 0.72, and K_m equals 1.2×10^{-4}. A typical graph of the determination of intrinsic viscosity is given below (Figure 7).

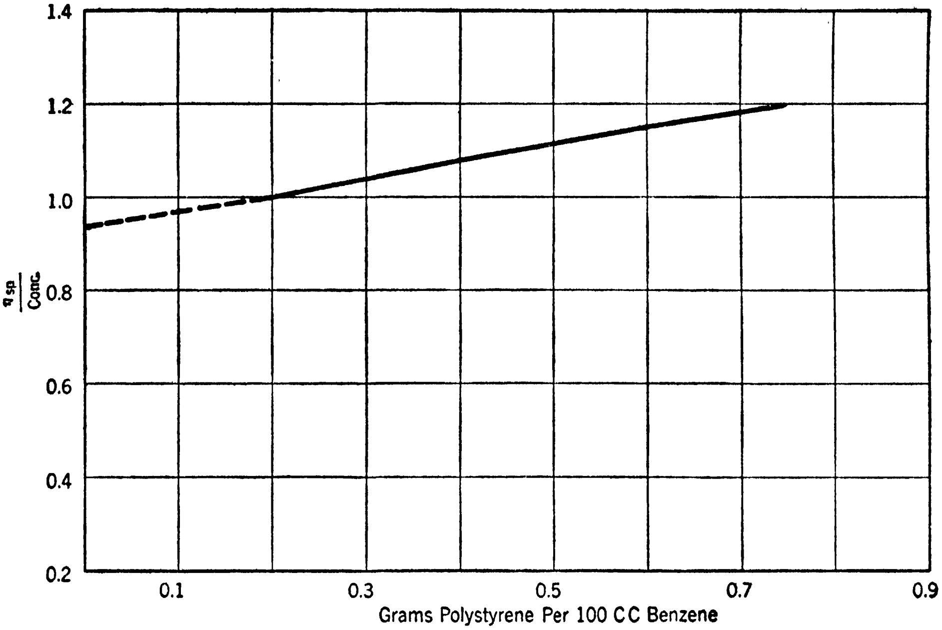


FIGURE 7. Determination of Intrinsic Viscosity

Plot percentage of catalyst against molecular weight for 24 hours' heating; for 144 hours' heating.

Using sample 1 of polystyrene throughout, determine the viscosity on 0.2, 0.4, 0.6, 1.0, 2.5, 5.0, and 10.0% solutions and plot (*a*) viscosity versus the concentration and (*b*) viscosity per concentration versus concentration.

Part C. Solvent Polymerization

Prepare ten screw-capped vials containing 5 grams of freshly distilled monomeric styrene, 15 grams of xylene, and 0.05 gram of benzoyl peroxide. Place the vials in a suitable oven or bath at 80° C for the indicated period of time and then remove from the oven and allow to cool to room temperature. When cool, pour the contents of the vial slowly and with rapid stirring into 50 cc of methyl alcohol in a 250-cc beaker. Wash the vial with as much methyl alcohol as is necessary to remove all the polymer from the vial and pour the washings of the vial into the beaker containing the precipitated polystyrene and methyl alcohol. Stir the precipitated polymer until it is completely disintegrated and all the xylene and unconverted monomer have been removed. Let the fine precipitated polymer stand for at least 2 hours before it is removed by filtration and wash the precipitate again with 25 cc of methyl alcohol. Dry the precipitate for at least 48 hours at 60° C or in a vacuum oven at the same temperature if one is available. When dry, weigh the precipitate and plot the amount of polymer obtained versus the time in hours.

Vial	*Time in Hours*	*Amount of Polymer*	*% Conversion*
1	0	....	....
2	0.5	....	....
3	1	....	....
4	2	....	....
5	4	....	....
6	6	....	....
7	24	....	....
8	72	....	....
9	144	....	....
10	240	....	....

Part D. "Pearl" Polymerization of Polystyrene

In a three-necked flask heated by a water bath and equipped with a thermometer, reflux condenser, and a variable speed air or electric motor stirrer, place 300 cc of distilled water. Start the stirrer and to the water add 0.5 gram of medium-viscosity polyvinyl alcohol, and stir to dissolve the polyvinyl alcohol, heating the water to 60 to 70° C if necessary. When the polyvinyl alcohol has dissolved, add 50 grams of redistilled styrene, in which 0.5 gram of benzoyl peroxide has previously been dissolved. Adjust the speed of the stirrer so that the styrene is dispersed into spheres or "pearls" and so as to prevent coalescence of the spheres. Heat the reaction flask to 85 to 90° C. *Throughout the process the stirring cannot be stopped.* During the early stages of polymerization any spheres that coalesce are easily broken up by the continued stirring, but as polymerization progresses and as polymer is formed in the globule, the spheres tend to become cohesive and *the stirring speed must be adjusted to prevent coalescence.* As the globules become harder, the tendency to ball and stick together decreases. Continue the heating for 7 to 8 hours and allow the reaction to cool to room temperature while the stirring is maintained. When cool, filter off the pearls, wash by immersion in 200 cc of methyl alcohol, and stir for 2 hours. Filter the beads from the methyl alcohol and dry at 50° C or in a vacuum oven at the same temperature. Examine the beads and note their shape and uniformity. Bounce a few of the beads and note their rather elastic nature.

Part E. Emulsion Polymerization of Styrene

Using the equipment of the "pearl" polymerization method dissolve 15 grams of Aerosol OT in 300 grams of distilled water and add to the reaction flask 50 cc of freshly distilled styrene, in which 0.5 gram of benzoyl peroxide has previously been dissolved. Start the stirrer and heat the contents of the flask at 85 to 90° C for 7 to 8 hours. Cool to room temperature, bottle, and examine the appearance and stability of the emulsion. Paint a sample of the emulsion on a piece of glass and let evaporate to a condition of dryness to the touch at room temperature, and then bake for one hour at 90° C. Cool the film and test its solubility in cold water.

Dilute 25 cc of the emulsion with 50 cc of water and precipitate the resin, while stirring, by the addition of a saturated sodium chloride solution. Filter the precipitate and wash three or four times with 250 cc of warm water. Treat with methyl alcohol as in the pearl polymerization method and dry at 50 to 60° C, preferably in a vacuum oven.

QUESTIONS

1. Why does increasing the catalyst decrease the molecular weight?
2. Discuss why the viscosity-concentration relationship is not a straight line.
3. Write the structure of polystyrene.
4. What is branching?
5. By what means may molecular weight be determined?
6. Give the commercial preparation of styrene. Give the laboratory preparation with benzaldehyde and acetic anhydride; and with phenyl ethyl alcohol.
7. Describe the advantages of the "Pearl" method over the mass emulsion or solvent polymerization.

Suggested Extensions

1. Investigate the effect of varying polymerization temperatures on molecular weights, with zero catalyst and with a constant catalyst percentage and constant time of polymerization.
2. Investigate more thoroughly the effect of varying polymerization time with constant catalyst percentage and constant temperature.
3. Investigate more completely the effect of varying percentage of catalyst with constant polymerization time and temperature.

EXPERIMENT 42

PREPARATION OF DIVINYLBENZENE POLYMERS AND COPOLYMERS

Part A. The Comparison of Styrene and Divinylbenzene

In screw-cap vials place 0.05 gram of benzoyl peroxide together with the indicated monomers. If the *p*-divinylbenzene is not available, the ortho and meta derivatives may be employed. If the divinylbenzene is available only in a diethylbenzene solution, e.g., in a 10 to 20% solution, the styrene should likewise be diluted with diethylbenzene to the same concentration and the polymerization carried out at 70° C for 144 hours. Polymerize as follows:

Vial	*Monomer*	
1	Styrene	5 grams or its equivalent diethylbenzene solution
2	*p*-divinylbenzene	5 grams or its equivalent diethylbenzene solution

Part B. A Copolymer Series of Styrene and Divinylbenzene

In screw-cap vials place 0.1 gram of benzoyl peroxide and add the monomers as given in the table below. An undiluted styrene and divinylbenzene must be used for this part of the experiment.

				Changes in Solubility and Swelling	
Vial	*Styrene*	*Divinylbenzene*	*Appearance*	*24 Hours*	*168 Hours*
1	10.0 grams	0.0 gram	....	....	....
2	9.9 grams	0.1 gram	....	....	....
3	9.7 grams	0.3 gram	....	....	....
4	9.5 grams	0.5 gram	....	....	....
5	9.0 grams	1.0 gram	....	....	....
6	7.0 grams	3.0 grams	....	....	....
7	5.0 grams	5.0 grams	....	....	....
8	3.0 grams	7.0 grams	....	....	....
9	1.0 gram	9.0 grams	....	....	....
10	0.0 gram	10.0 grams	....	....	....

Polymerize each of the mixtures at 70° for 24 hours, 80° for 24 hours, 100° for 24 hours, and 125° C for 72 hours. When the polymerization is complete, fracture the vial, and remove the casting completely. Place the castings in 50-cc test tubes marked 1 to 10 to correspond to the composition in the vial. Introduce 15 cc of benzene into each test tube and stopper lightly to prevent evaporation of the benzene. Observe the change in swelling in 24 and 168 hours, and indicate the change qualitatively by expressing the swelling as a percentage increase of the original casting.

Part C. Partial Polymers of Divinylbenzene

In a round-bottomed flask equipped with condensers, reflux the following mixtures for the stated times. If gelation occurs before this time, stop the reaction and repeat the experiment, using reflux times short of the gelation time.

	Parts of 18–22% Divinylbenzene Solution in Diethylbenzene	*Benzene*	*Parts Bz_2O_2*	*Time, Minutes*
Flask 1	100	0	0.20	25
Flask 2	100	100	0.20	25

If the contents of the second flask do not gel, cool, and pour the solution slowly and with stirring into 500 cc of 95% ethyl alcohol to precipitate the partial polymer. Filter the polymer, wash with more ethyl alcohol, dry at room temperature or in a vacuum oven at 35° C, and grind to a fine powder. Test its solubility in benzene, acetone, and dioxane, and select a suitable solvent from this group to prepare a 10% solution of partial polymer containing 2% benzoyl peroxide as based on the actual polymer content. Pour a film of this varnish on glass and bake for 2 hours at 130° C. Test the solubility of the heat-treated film in benzene, acetone, and dioxane.

Part D. Copolymers of Divinylbenzene with Maleic Esters

Prepare the following solutions in round-bottomed flasks equipped for reflux and determine the gelation time as controlled by the amount of diethyl maleate in the composition.

	Parts of 18–20% Divinylbenzene Solution in Diethylbenzene	*Parts Diethyl Maleate*	*Bz_2O_2*	*Gelation Time*
Flask 1	100	0	0.20	....
Flask 2	100	25	0.20	....
Flask 3	100	50	0.20	....
Flask 4	100	75	0.20	....

If desired, the soluble, fusible polymer may be isolated by stopping the reaction short of gelation and precipitating the partial polymer in ethyl alcohol.

QUESTIONS

1. Discuss the differences in the solubility of the polymers of styrene and divinylbenzene from the standpoint of the structure of their monomers.
2. How does the concentration of divinylbenzene affect the swelling and solubility of a styrene copolymer?
3. Describe what has occurred on heat-treating a film of the partial polymer of divinylbenzene.
4. Write the structural formulas for the polymerization product of (*a*) one mole of styrene with one mole of dimethyl maleate; (*b*) one mole of divinylbenzene with one mole of dimethyl maleate.

EXPERIMENT 43

PREPARATION OF A METHACRYLIC ESTER

In a three-necked, 1-liter flask, heated by a suitable bath and fitted with a stirrer, reflux condenser, and thermometer, place 180 grams of tricresyl phosphate, 21.5 grams of phosphorus pentoxide, and 0.2 gram of copper bronze powder. Stir the mixture until a partial solution is formed and, with stirring, slowly add 60 grams of ethyl or methyl α-hydroxyisobutyrate, maintaining the temperature below 65° C until the addition is complete. After the addition of the isobutyrate, raise the temperature to a point between 80 and 100° C and maintain at that temperature for 3 hours.

After the reaction has been completed, adjust the reflux condenser for downward distillation. Distill into a cooled receiver all the material boiling up to 170° C. The distillate is the crude methacrylic ester. Wash the distillate with 10% aqueous sodium carbonate and dry over anhydrous sodium sulfate. Redistill the methacrylate ester in the presence of a small amount of copper powder to inhibit the polymerization. Collect for further use the fraction boiling between 97 and 103° C as methyl methacrylate and the fraction boiling between 115 and 120° C as ethyl methacrylate. Record the following data:

	Boiling Point	*Refractive Index*
Methyl methacrylate	....	....
Ethyl methacrylate	....	....

Bottle, weigh, and label the product. Store the ester in a refrigerator if it is not to be used immediately.

QUESTIONS

1. Write the complete synthesis of ethyl methacrylate, starting with acetone.
2. How is acetone prepared from gaseous petroleum products?
3. Why is the methacrylate stored in a refrigerator? What happens if a sample is left exposed to sunlight?
4. Can the polymerization reaction be inhibited? If so, name at least three effective inhibitors.

EXPERIMENT 44

POLYMERIZATION OF A METHACRYLIC ESTER

Part A. Thermal Polymerization

Using methyl or ethyl methacrylate, introduce the following 5-gram samples in small screw-capped vials containing varying percentages of benzoyl peroxide, and observe the polymerizations at the end of 12 hours, 24 hours, 48 hours, and 5 days when heated at a temperature of 60° C. Describe the polymers as slightly viscous, highly viscous, viscous gel, rubbery, solid, etc.

	Benzoyl Peroxide		*Observations*			
Sample	*Weight*	*Percentage*	*6 Hours*	*12 Hours*	*24 or 48 Hours*	*5 Days*
1	0.000	0.0	....	....	....	....
2	0.005	0.1	....	....	....	....
3	0.025	0.5	....	....	....	....
4	0.05	1.0	....	....	....	....

Part B. Ultraviolet Polymerization

Prepare four samples as in Part *A* and expose them either to sunlight or to the ultraviolet light of a mercury arc or fluorescent lamp. Observe the results and record as in Part *A*.

	Benzoyl Peroxide		*Observations*			
Sample	*Weight*	*Percentage*	*6 Hours*	*12 Hours*	*24 or 48 Hours*	*5 Days*
1	0.000	0.0	....	....	....	....
2	0.005	0.1	....	....	....	....
3	0.025	0.5	....	....	....	....
4	0.05	1.0	....	....	....	....

QUESTIONS

1. Contrast the two polymerization methods and the results.
2. How does the catalyst concentration affect the polymerization and the molecular weight?
3. Is ultraviolet light an activator of polymerization?

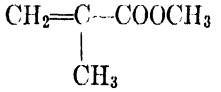
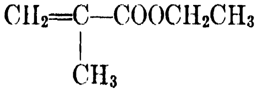
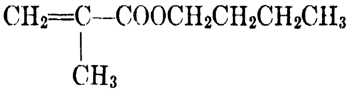
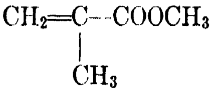
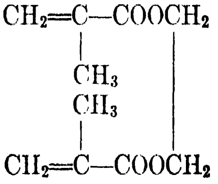
Suggested Extension

1. Refer to the literature for the published value of K_m for the methacrylic esters, and compare the molecular weights obtained by each of these methods.

EXPERIMENT 45

PROPERTIES VERSUS CONSTITUTION IN THE ACRYLIC SERIES

To each of the following inhibitor-free monomers add 0.1% benzoyl peroxide. and polymerize the mixture at 50° C for 7 days.

	Sample	*Monomer*	*Structure*	*Empirical Formula*
Group A	1	Methyl acrylate	$CH_2{=}CH{-}COOCH_3$	$C_4H_6O_2$
	2	Ethyl acrylate	$CH_2{=}CH{-}COOCH_2CH_3$	$C_5H_8O_2$
	3	Methyl methacrylate	 $CH_2{=}C(CH_3){-}COOCH_3$	$C_5H_8O_2$
	4	Ethyl methacrylate	 $CH_2{=}C(CH_3){-}COOCH_2CH_3$	$C_6H_{10}O_2$
	5	Butyl methacrylate	 $CH_2{=}C(CH_3){-}COOCH_2CH_2CH_2CH_3$	$C_8H_{14}O_2$
Group B	6	Methyl methacrylate	 $CH_2{=}C(CH_3){-}COOCH_3$	$C_5H_8O_2$
	7	Glycol dimethacrylate	 $CH_2{=}C(CH_3){-}COOCH_2{-}CH_2OOC{-}C(CH_3){=}CH_2$	$(C_5H_7O_2)_2$

Tests. Test the polymers for heat resistance at 70°, 100°, and 150° C and immerse samples of the polymers in alcohol, acetone, ethyl acetate, petroleum ether, etc., to determine solvent resistance. If the monomers are not available, the butyl and glycol dimethacrylate may be prepared from methyl or ethyl methacrylate by ester-exchange reactions.

QUESTIONS

1. Record from the literature the physical properties of the monomers and polymers of this experiment.
2. Describe qualitatively the thermal and solvent properties of the series of polymers prepared.
3. Explain all results obtained in relation to the structure of the monomers and polymers.
4. Describe the ester-exchange reaction in terms of a generalized equation. Give at least two literature references to this ester-exchange reaction.
5. Explain the fundamental differences in the results obtained from Group *A* and Group *B*.

EXPERIMENT 46

CROSS-LINKED METHACRYLATE POLYMERS

Part A. Cross-Linked Copolymers of Methyl Methacrylate

Prepare a series of 10-gram castings in small test tubes or screw-capped vials containing 0.01 gram of benzoyl peroxide and the following mixtures of inhibitor-free methyl methacrylate and glycol dimethacrylate or other polyhydric alcohol methacrylate esters.*

Sample	*% Methyl Methacrylate*	*% Glycol Dimethacrylate*
1	100	0
2	95	5
3	90	10
4	50	50
5	20	80
6	5	95
7	0	100

Cast the samples at 60° C for 48 hours. Follow this by raising the temperature to 80° C for 48 hours, and after this continue the heating at 110° C for an additional 48 hours.

Tests. Heat the polymers to 130° C, and note their condition after the end of an hour. Test their heat resistance by applying pressure by means of pliers or tongs to the heated samples.

Part B. Preparation of Partial Polymer of Glycol Dimethacrylate

Reflux the mixture of the following ingredients for 1 to 1½ hours.

Glycol dimethacrylate *	10 grams
Benzoyl peroxide	0.7 gram
Acetone	60 cc

At the end of the reflux time pour the mixture, with stirring, into 750 to 1000 cc of methyl alcohol and allow the precipitate formed to settle. Filter off the precipitate and dry at room temperature. If premature gelation occurs, repeat the experiment, reducing the reflux time or the amount of catalyst.

Test the solubility of the precipitate in methyl methacrylate and prepare a copolymer of methyl methacrylate, 95 parts, and glycol dimethacrylate partial polymer, 5 parts, for heat-resistance comparison with sample 2, Part *A*.

QUESTIONS

1. Describe qualitatively the condition of the copolymers at 130° C.
2. How does the surface hardness change as the cross-linking agent is increased in the copolymers?
3. Does a high amount of cross-linking increase the brittleness of the copolymers?
4. Predict the effect of methallyl methacrylate in a methyl methacrylate polymerization product.

---

* If glycol dimethacrylate is unavailable, methacrylic anhydride may be used in this experiment.

EXPERIMENT 47

CROSS-LINKED GELS USING METHACRYLATE ESTERS

Prepare the following compositions by weight in grams:

Material	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Pentachlorodiphenyl	18	18	15	12	9	6	3	19.9
Styrene	2	1.9	4.9	7.9	10.9	13.9	16.9	0.0
Glycol dimethacrylate *	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Benzyl peroxide	0.2	0.02	0.05	0.08	0.10	0.14	0.17	0.02

* Divinylbenzene, methacrylic anhydride, or any other polyhydric alcohol ester of methacrylic acid may be used in these experiments if glycol dimethacrylate is not available.

Heat the mixtures at 50° C for 24 hours, and continue the heating at 75° C for 24 hours and then at 100° C for 24 hours. Test the fusibility of the gel at 120° C and record a qualitative value of stiffness at this temperature, using 10 as the highest value, 1 as the lowest, and 0 as none. Place 0.5 gram of each of the polymerized samples in 20 cc of benzene for 24 hours. Note the condition of the sample, decant the benzene, or filter off the undissolved solid and dry it at 80° C for 24 hours. Reweigh the sample and calculate the percentage lost.

Sample	*Fusibility*	*Stiffness*	*Relative Swelling*	*% Extractable Gel*
A	....	....	....	....
B	....	....	....	....
C	....	....	....	....
D	....	....	....	....
E	....	....	....	....
F	....	....	....	....
G	....	....	....	....
H	....	....	....	....

QUESTION

1. What is the physical nature of the gel and how does it change with the composition?

EXPERIMENT 48

SUBSTITUTED ACRYLIC ESTERS—THE CHLOROACRYLIC ESTERS

Part A. The Preparation of Methyl α,β-Dichloroproprionate

In a three-necked flask, equipped with a reflux condenser, stirrer, thermometer, and a gas inlet tube, place 200 grams of methyl acrylate, 80 grams of dry methyl alcohol, and 1.5 grams of hydroquinone. Weigh the flask and its contents. Cool this mixture in an ice bath to 10 to 15° C, and with vigorous stirring pass in the gaseous chlorine slowly, at such a rate that all the chlorine is absorbed and the temperature does not rise above 20° C. Cool the reaction mixture with an ice bath if necessary. When the calculated amount of chlorine has been absorbed, as determined by weight increase of the flask, transfer the product to a vacuum distilling apparatus and distill through a 1-foot glass-bead-packed column at 20 mm pressure. Collect as methyl dichloroproprionate the fraction boiling between 72 to 75° C at 20 mm. Yield ______ grams, ______ % theoretical.

Part B. Dehydrohalogenation

In a suitable reflux flask mix the following ingredients in the ratios indicated.

Methyl α,β-dichloroproprionate	100 grams
Quinoline	105 grams
Hydroquinone	1 gram

Heat the mixture at 100° C for 15 minutes. Transfer the reaction product to a vacuum distilling apparatus, and distill at a pressure of 40 mm. Collecting as methyl α-chloroacrylate the fraction boiling between 58 and 60° C, wash the distillate twice with an equal volume of a 5% aqueous solution of hydrochloric acid, and twice with distilled water. Dry over anhydrous sodium carbonate, and filter. A yield of about 80% may be expected.

Polymerize a sample of the dry ester, using 0.25% benzoyl peroxide as a catalyst, at 50° C, for 10 days. Save the remainder of the ester for a future experiment.

QUESTIONS

1. Why is the chloroacrylic ester washed with HCl?
2. If sufficient hydroquinone is not present during the chlorination, rapid polymerization will result. Explain why this is so.

Suggested Extension

1. Prepare the bromoacrylic esters, and compare their polymerization and polymers to the chloroacrylate ester. Discuss why the bromo esters do not polymerize or copolymerize as well as the chloro derivatives.

EXPERIMENT 49

EFFECT OF INHIBITORS

To a sample of inhibitor-free methyl methacrylate add 0.2% by weight of benzoyl peroxide and the indicated amount of hydroquinone or pyrogallol. Polymerize this mixture at 70° C for one week. Then measure their molecular weights, using the viscosity method. What solvent should be used?

Sample	*Hydroquinone % by Weight*	*Molecular Weight or Relative Viscosity*
1	0.0	....
2	0.1	....
3	0.3	....
4	0.5	....
5	1.0	....
6	3.0	....
7	5.0	....
8	10.0	....

QUESTIONS

1. Discuss the effect of the inhibitor on the polymerization rate and on the molecular weight of the resulting polymer, and plot either molecular weight or relative viscosity versus percentage inhibitor.
2. What would you expect the effect of tetraethyl lead or triphenylmethyl to be on the polymerization rate and molecular weight of the polymer from methyl methacrylate?

Suggested Extensions

1. Study the effect of sulfur, copper, copper salts, and other metals and salts as inhibitors. What should be expected from aluminum chloride and boron trifluoride?
2. Study the effect of the higher mercaptans, e.g., decyl and dodecyl mercaptans in contrast with the lower alkyl mercaptans.

EXPERIMENT 50

PREPARATION OF POLYVINYL ACETATE

Part A. Emulsion Polymerization

In a 250-cc, three-necked flask, fitted with a mechanical stirrer and cork stoppers, place 100 cc of distilled water, 5 grams of Aerosol OT, and 0.1 gram of potassium persulfate. Stir the mixture until the solution is complete. To this mixture, add 20 grams of *freshly* distilled vinyl acetate. Stir the mixture vigorously until a dispersion is formed. Immerse the reaction vessel in a water bath maintained at 65° C and continue the stirring. After the temperature of the reacting mass reaches 60° C, and at the stated intervals thereafter, withdraw a sample of the emulsion and determine the resin content. Discontinue the reaction at the end of one hour at 60 to 65° C.

Sample	*% Resin Content*
0-minute	....
5-minute	....
30-minute	....
60-minute	....

Compare these values with the theoretical resin content.

Dilute 25 cc of the emulsion with 50 cc of water, and precipitate the resin, while stirring, by the addition of a saturated sodium chloride solution. Filter the precipitated resin, and wash three or four times with 250 cc of warm water. Dry overnight in a 50° C oven. Dissolve 0.5 gram of the dry resin in 100 cc of benzene, and measure its viscosity at 20° C. Pour some of the emulsion on a glass plate and permit it to dry at room temperature, followed by baking at 75° C for 3 hours. Cool to room temperature and test the solubility of the dried film in water. Precipitate the remainder of the emulsion, bottle, label, and store for future use.

Part B. Mass Polymerization

Polymerize 5 grams of freshly distilled vinyl acetate and 0.025 gram of benzoyl peroxide in a small vial at 50° C for 3 days. Dissolve 0.5 gram of the resin in 100 cc of benzene, and measure its viscosity at 20° C. Compare this value with that obtained in Part *A*.

QUESTIONS

1. Compare qualitatively the molecular weights of the two resins obtained by the emulsion and mass polymerization methods respectively.
2. Give the complete synthesis of vinyl acetate, starting with calcium carbide and inorganic chemicals.
3. What is ethylidene diacetate?
4. Write the reactions, showing how ethylidene diacetate may be a by-product of the vinyl acetate synthesis.
5. Discuss the industrial advantages of emulsion over mass polymerization, and compare it with solution polymerization.

Suggested Extensions

1. Using a constant amount of benzoyl peroxide and vinyl acetate, compare the molecular weights of the resulting polymers when polymerized as follows: (*a*) in mass, (*b*) in emulsion, and (*c*) in solution, e.g., in ethyl acetate and acetic acid.
2. Compare the molecular weights of polyvinyl acetate prepared in the following solutions: (*a*) in methyl acetate, (*b*) in ethyl acetate, (*c*) in benzene, (*d*) in acetic acid, and (*e*) in acetone.

EXPERIMENT 51

PREPARATION OF A POLYVINYL ALCOHOL

In a 1-liter, three-necked flask, fitted with a heavy-duty, mercury-sealed stirrer and reflux condenser, place 25 grams of polyvinyl acetate and 700 cc of absolute methyl alcohol. With stirring and heating at 75° C, dissolve the polyvinyl acetate in the methyl alcohol. Fit a gas bubble tube into the remaining neck of the flask, and pass anhydrous hydrogen chloride either from a cylinder or from a hydrogen chloride or salt-sulfuric acid generator into the reaction mixture, for a period of 2 hours. Stir the reaction mixture continuously, and at the end of the heating period remove the gas bubble tube and insert a dropping funnel. Adjust the stirring mechanism so that it is just hitting the liquid and splashing the solution onto the side of the flask. Raise the temperature to 85° C. Then add approximately 25 cc of 95% ethyl alcohol, while stirring is continued. A white powdery precipitate of polyvinyl alcohol will appear in the flask. Filter the solution with suction. Wash the precipitate thoroughly four times, using 50 cc of 95% alcohol per wash. Dry the polyvinyl alcohol at room temperature for 12 hours. Test and record the solubility of the product in water, methyl alcohol, ethyl alcohol, dioxane, acetone, benzene, and acetic acid, and compare the results to the solubilities of polyvinyl acetate.

	Solubility	
Solvent	*Polyvinyl Acetate*	*Polyvinyl Alcohol*
Water	....	....
Methyl alcohol	....	....
Ethyl alcohol	....	....
Dioxane	....	....
Acetone	....	....
Acetic acid	....	....
Benzene	....	....
Ethylene glycol	....	....

QUESTIONS

1. Write the equation for the ester exchange reaction between polyvinyl acetate and methyl alcohol.
2. Discuss the solubility of polyvinyl alcohol in the systems: H—OH, CH_3—OH, HO—CH_2—CH_2—OH.

Suggested Extensions

1. Reacetylate the polyvinyl alcohol. Determine the molecular weight of the reacetylated sample, and compare this with the original sample of polyvinyl acetate. Has any degradation occurred? Compare this with the system: cellulose to cellulose acetate to cellulose.
2. Using one lot of polyvinyl acetate, compare the polyvinyl alcohol prepared from it under acid and alkaline conditions of hydrolysis.

EXPERIMENT 52

PREPARATION OF A POLYVINYLFORMAL

In a three-necked, 1-liter flask fitted with a reflux condenser and a slow powerful stirrer, place 50 grams of polyvinyl acetate and 93 grams of glacial acetic acid. With stirring, dissolve the polyvinyl acetate in the acetic acid. Then add to this solution 42 grams of formalin (37.1% by weight of formaldehyde) in which has been dissolved 3.4 grams of concentrated sulfuric acid.

Heat the stirred mixture for 24 hours, using a suitable water bath maintained at a temperature of 75 ± 5° C. At the given time intervals, sample the solution, titrate for acidity, and for formaldehyde content, using Test Method 22, and record the data in the following table.

Time, Hours	*Equivalents of Acid*	*Equivalents of Formaldehyde*
0	....	....
5	....	....
10	....	....
20	....	....
24	....	....

At the end of the 24 hours, pour the solution into a beaker, fitted with a fast stirrer, and add water very, very slowly until the mass becomes opalescent and finally precipitates in fine granules. Filter off the granules. Wash the granules with 500 cc of distilled water, then, with 500 cc of 1% aqueous ammonium hydroxide, and, finally, with 1000 cc of distilled water. Dry for 12 hours at 60° C. Determine the solubility of the dried resin in dioxane, acetic acid, phenol, cresol, and the other solvents listed below. Analyze the product for acetyl groups (Test Method 23), hydroxyl groups (Test Method 24), formal groups (Test Method 25) and record the data as follows:

Solvent	*Solubility*
Phenol	....
Cresol	....
Dioxane	....
Acetic acid	....
Benzene	....
Water	....
Methyl alcohol	....
Ethyl alcohol	....
Acetone	....

Tests

Acetyl groups ....

Hydroxyl groups ....

Formal groups ....

QUESTIONS

1. Write the equations for the formation and structure of a polyvinylformal resin.
2. The chemical reaction for formalization is the same whether cyclization in the same chain or cross-linkage between different chains occurs. On the basis of your solubility results, and in contrast with polyvinyl acetate, do you believe that much cross-linking has occurred?

Suggested Extensions

1. Study the properties of the formal as a function of hydroxyl, acetyl, and formal groups.
2. Prepare the formal in the presence of other aldehyde reactive substances such as phenol, cresol, and urea.

EXPERIMENT 53

PREPARATION AND PROPERTIES OF A POLYVINYLBUTYRAL

Part A. Preparation of Polyvinylbutyral

(1) Liquid Phase Preparation. Carry out this reaction in a manner similar to that used in the preparation of polyvinylformal. In this case use 22 parts by weight of polyvinyl alcohol, dissolved in 100 parts by weight of glacial acetic acid, to which has been added 32 parts of pure redistilled butyraldehyde. When these materials are thoroughly mixed, add 3 parts by weight of concentrated hydrochloric acid dissolved in 10 parts by weight of water. Allow the mixture to react at 50° C, as in the preparation of the polyvinylformal. At the end of 12 hours, precipitate with water, wash, and dry at 50° C. Analyze the product by Test Methods 23 and 24, and report the hydroxyl and acetyl groups. Test the product for solubility in benzene, ethyl alcohol, dioxane, and butyl alcohol, and report the data as follows:

Solvent	*Solubility*
Dioxane	....
Benzene	....
Ethyl alcohol	....
Butyl alcohol	....
Tests	
Hydroxy groups	....
Acetyl groups	....
Butyral groups	....

Bottle and label the resin for a future experiment.

(2) Solid Phase Preparation. In a 1-liter flask equipped with a thermometer, reflux condenser, and stirrer, and a Stark and Dean trap, in a suitable heating bath (Figure 6), introduce 500 cc of heptane, 35 grams of butyraldehyde, 3 grams of oxalic acid, and 44 grams of polyvinyl alcohol. Start the stirrer and heat the reaction mixture to reflux. Continue the heating until the water of reaction has been collected, allow the reaction to cool, and then filter off the polyvinylbutyral *in the absence of flame* and air-dry the polymer. Disperse the air-dried polymer in 500 cc of water in a beaker on an electric hot plate, and, with stirring, boil the mixture for one-half hour to eliminate dissolved aldehyde and retained heptane. Filter the polymer and dry at 50 to 60° C in a vacuum oven. Compare the solubility and other properties of this polymer to the one prepared in solution.

Part B. Comparison of Polyvinylformal and Polyvinylbutyral

By blending in a beaker or tumbling barrel prepare the following compositions:

1. Polyvinylformal	60 parts
Diethylene glycol dihexoate or dibutyl sebacate	40 parts
2. Polyvinylbutyral (Part *A*, resin 1)	60 parts
Diethylene glycol dihexoate or dibutyl sebacate	40 parts
3. Polyvinylbutyral (Part *A*, resin 2)	60 parts
Diethylene glycol dihexoate	40 parts

Process the mixture on milling rolls, with the front roll heated with 15 to 20 pounds of steam and the rear roll kept cool with running water. Mill the mixture for approximately 5 minutes after a uniform sheet is obtained. Compare the three plasticized materials as to flexibility, hardness, elasticity, etc.

QUESTIONS

1. Should the formal or the butyral be used as a safety glass interliner?
2. Discuss the differences in the liquid and solid phase preparation of the butyral.

Suggested Extensions

1. Study the properties of the polymer as a function of the hydroxyl and butyral content.
2. Study the physical properties versus the plasticizer content.
3. Study the convertibility of the polyvinylbutyral by the addition of (*a*) phenol-aldehyde resins, (*b*) substituted phenol-aldehyde resins, (*c*) butylated urea and melamine resins.
4. Prepare mixed derivatives of polyvinyl alcohol using two aldehydes, e.g., formaldehyde and butyraldehyde, either simultaneously or consecutively.

PREPARATION OF VINYL CHLORIDE MONOMER

Assemble the apparatus as pictured in Figure 8, using a three-necked 500-cc flask equipped with a stirrer with mercury seal, thermometer, dropping funnel, and a reflux condenser. Attached to the top of the reflux condenser is a second condenser set downward for distillation and leading into a flask immersed in an acetone and dry-ice bath. Introduce about 100 cc of methyl alcohol into the flask and add 80 grams of C.P. sodium hydroxide pellets. If the methyl alcohol is insufficient to cover the sodium hydroxide, more methyl alcohol must be added. Make sure that the collection flask is cooled by immersion in the dry-ice bath before continuing with the experiment; otherwise, the vinyl chloride prepared will be lost for lack of condensation. The stirrer is started, and the flask heated to about 50° C on a steam bath or with an electric heater.

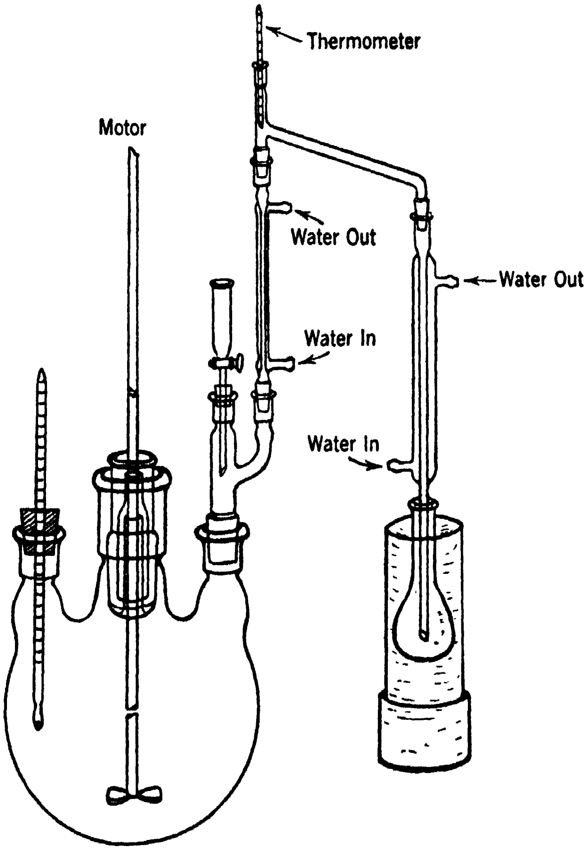


FIGURE 8. Vinyl Chloride Apparatus.

Caution. Do not use a gas flame as vinyl chloride monomer is highly inflammable and explosive. Make sure cold water is running through both condensers. Preferably, this experiment should be carried out under a hood.

Place 215 grams of redistilled ethylene dichloride in a separatory funnel and add it dropwise to the methanol-sodium hydroxide mixture from the dropping funnel at the rate of about 100 drops a minute. The heating of the flask is continued until a temperature of about 70° C is reached, at which point the heat is removed since the heat of reaction will continue supplying sufficient energy. If the reaction temperature drops, supply heat to the reaction flask to maintain it at about 70° C. Methyl alcohol and ethylene dichloride are refluxed in the reflux condenser and returned to the reaction flask while the vinyl chloride passes on to the cooling flask. If the temperature as indicated by the thermometer placed in the reflux condenser rises higher than room temperature, the heat on the reaction flask should be reduced or the rate of addition of ethylene dichloride decreased. Stirring is continued at a moderately slow rate throughout the reaction.

For further use, the liquefied vinyl chloride monomer which has been cooled in the receiving flask is redistilled as follows to eliminate any ethylene dichloride and methyl alcohol which may have been carried over. Detach the three-necked flask from the reflux condenser and remove the receiving flask containing the liquefied vinyl chloride from the dry-ice bath and attach it to the open bottom of the reflux condenser, then introduce a clean receiving flask into the dry-ice bath. The redistillation of the vinyl chloride is effected, allowing the flask containing the liquefied vinyl chloride to warm up to room temperature. Further application of heat is unnecessary. The redistilled vinyl chloride is used as soon as possible after its preparation. Record the boiling point of the redistilled vinyl chloride, the theoretical yield, and the actual yield.

QUESTIONS

1. Compare the formulas and boiling points of vinyl chloride with ethyl chloride, symmetrical dichloroethylene, asymmetrical dichloroethylene, ethylene dichloride, trichloroethylene, and tetrachloroethylene.
2. Compare the polymerizability of the unsaturated chlorinated ethylenes.
3. Write the reactions for the preparation of vinyl chloride, starting with only inorganic materials.
4. Give the equations for the synthesis of vinyl iodide, vinyl bromide, and vinyl fluoride, and compare the tendency and rates of polymerization of these monomers with vinyl chloride.
5. What side reactions may take place in the system ethylene dichloride, methyl alcohol, and sodium hydroxide?

Suggested Extensions

1. Study the use of other alkalies such as potassium hydroxide, calcium hydroxide, etc., on the dehydrohalogenation of ethylene dichloride.
2. Study the preparation of vinyl chloride from ethylene dichloride and sodium or potassium hydroxide in an aqueous system.
3. Prepare vinyl chloride from acetylene and hydrogen chloride, using as a catalyst mercuric chloride absorbed on active charcoal in the absence and presence of KCl, $BaCl_2$, Hg, etc.

EXPERIMENT 55

ULTRAVIOLET POLYMERIZATION OF VINYL CHLORIDE

Part A. Preparation of Polymer

As a reaction chamber, use a Pyrex glass tube 12 inches long, with an inside diameter of about 15 mm, sealed at one end. This tube is graduated to a 20-cc volume to enable the worker to measure out 20 cc of vinyl chloride by condensation of this gas directly within the tube.

Introduce 0.02 gram of benzoyl peroxide into the tube by means of a long-stemmed funnel to prevent its accumulation on the walls of the tube. Immerse the glass tube in a dry-ice-chloroform-carbon tetrachloride bath in a thermos flask, and allow the tube to cool to the temperature of the bath. In the absence of flames, condense about 20 cc of vinyl chloride directly into the Pyrex tube from a cylinder or a reservoir of vinyl chloride. Protect your eyes with safety goggles, and seal the open end of the tube while it is still in the cooling bath. Remove the tube from the bath, and allow it to warm up to room temperature. Expose the sealed tube to sunlight or to a mercury arc lamp until all the liquid vinyl chloride has been converted to a white powder. To remove the polymer, cool the tube in a dry-ice bath, wrap it in a piece of heavy canvas, and crack the glass with a heavy metal object. Separate the polymer from the glass, and use it for viscosity measurements.

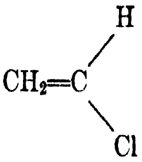
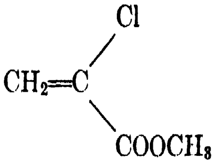
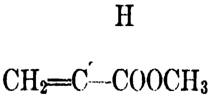
Part B. Molecular Weights of Polyvinyl Chloride

Refer to Experiment 41, and, using the value of K_m as 1.1×10^{-5} and a equals 1, calculate the molecular weight of a sample of commercial polyvinyl chloride. Compare this value with that of a laboratory-prepared polymer. Employ redistilled cyclohexanone as the solvent. Record the data in the following table:

	Molecular Weight
Laboratory sample	....
Commercial sample	....

QUESTIONS

1. How is vinyl chloride prepared industrially? List the catalysts used in its preparation. What by-products are obtained?
2. Give two syntheses for the preparation of vinyl chloride from ethylene.
3. What is vinylidene chloride? How is it prepared?
4. Plan, and submit for your instructor's approval, a series of tests with the polymers of the previous experiments which will show the similarities and differences of the polymers of the three monomers listed below, with particular reference to the structure of the monomers.

1. Vinyl chloride, 
2. Methyl α-chloroacrylate, 
3. Methyl acrylate,  $CH_2{=}\overset{H}{C}{-}COOCH_3$

Suggested Extension

1. Repeat the experiment, omitting the benzoyl peroxide, and compare the yield and the time of polymerization with samples containing varying quantities of benzoyl peroxide.

EXPERIMENT 56

COPOLYMERS OF VINYL CHLORIDE

Part A. Emulsion Copolymerization with Vinyl Acetate

As reaction chambers, use Pyrex glass tubes 12 inches long, with an inside diameter of 15 mm, and sealed at one end. These tubes should be graduated in 1-cc steps for a total of 10 cc to enable the worker to measure out a definite quantity of reactants. To prevent accumulation of substances on the walls of the tubes, use a long-stemmed funnel to introduce into each tube 0.03 gram of benzoyl peroxide and then varying amounts of redistilled vinyl acetate as indicated below. *Use safety goggles* to protect your eyes throughout the experiment. Immerse the glass tubes in a dry-ice bath, and, in the absence of flames, condense into each tube the indicated amount of vinyl chloride to make a 10-cc volume. Next add 20 cc of refrigerator-cooled dispersing agent prepared by dissolving 3 grams of Aerosol OT in 150 cc of distilled water. Seal the open ends of the tubes. Remove the tubes from the cooling mixture and allow them to warm to room temperature. Shake the sealed tubes to disperse the materials. Polymerize the mixture in the tubes for 5 to 6 days by heating the tubes in a constant temperature water or air bath at 40 to 50° C, using tumbling or shaking attachments if available. Polymerize the following mixtures:

Tube	*Vinyl Acetate*	*Vinyl Chloride*	*Yield in Grams*
0	0	10 cc	....
1	1 cc	9 cc	....
2	3 cc	7 cc	....
3	5 cc	5 cc	....
4	7 cc	3 cc	....
5	9 cc	1 cc	....
6	10 cc	0	....

At the end of the polymerization time remove the tubes from the bath, *protecting your eyes* with *safety goggles.* Cool the tubes in a dry-ice bath. Open the tubes by directing a flame at the top end of the tube which is held vertically. As soon as a puncture has been made in the tube, it can be opened further by spreading with a file. Pour the polymers into beakers, and precipitate the dispersion completely with a saturated sodium chloride solution. Filter off the precipitated polymers, wash thoroughly with distilled water, and dry at 50° C. Record the yields obtained.

Part B. Evaluation of the Polymers

Mold each of the materials in a small mold, and test each product for impact and flexural strength. Since the amount of material will be small, these properties should be tested with a Dynstat apparatus if one is available. If such equipment is not available, give a qualitative description of the polymers prepared. Note the color of the samples and their solubilities in methyl ethyl ketone. Record the data in the following form:

Sample from Tube	*Color*	*Solubility*	*Flexural Strength*	*Impact Energy Foot-Pounds*	*Description of Polymer*
0	....	....	....	....	....
1	....	....	....	....	....
2	....	....	....	....	....
3	....	....	....	....	....
4	....	....	....	....	....
5	....	....	....	....	....
6	....	....	....	....	....

Part C. Emulsion Copolymerization with Methyl Acrylate

Methyl acrylate is an isomer of vinyl acetate, as may be noted from the structural formulas:

$CH_2{=}CH{-}COOCH_3$
Methyl acrylate

$CH_2{=}CH{-}O{-}COCH_3$
Vinyl acetate

Using *redistilled* methyl acrylate instead of vinyl acetate, repeat Part *A* of this experiment. Compare the properties and solubilities of the acrylate copolymers with the vinyl acetate copolymers.

QUESTIONS

1. Discuss the copolymers obtained and show evidence that copolymerization has occurred.
2. Write the general structure of a 9-to-1 copolymer of vinyl chloride and vinyl acetate.
3. How does the vinyl acetate affect the (*a*) stiffness of the copolymer, (*b*) the solubility, and (*c*) the softening point?

EXPERIMENT 57

PREPARATION OF PLASTICIZED POLYVINYL CHLORIDE

Plasticize the following lots of commercial polyvinyl chloride and commercial polyvinyl chloride-acetate copolymer with the amounts of tricresyl phosphate indicated in the following table:

Lot	*Commercial Polyvinyl Chloride*	*Tricresyl Phosphate*	*Lot*	*Commercial Polyvinyl Chloride Copolymer*	*Tricresyl Phosphate*
1	100 parts	0 parts	*1C*	100 parts	0 parts
2	80 parts	20 parts	*2C*	80 parts	20 parts
3	60 parts	40 parts	*3C*	60 parts	40 parts
4	50 parts	50 parts	*4C*	50 parts	50 parts
5	40 parts	60 parts	*5C*	40 parts	60 parts

Blend the polymers and the tricresyl phosphate in a beaker prior to placing the mixtures on milling rolls. The front roll should be heated with 15 to 20 pounds of steam, and the rear roll maintained cool by running water. Mill the compounds for approximately 5 minutes after uniformity is obtained.

Describe qualitatively the elasticity and the general characteristics of the plasticized polymers. Note also whether the polymer or the copolymer processes more readily during milling.

QUESTIONS

1. How does the elasticity vary as a function of plasticizer content?
2. Does the same amount of plasticizer produce softer compositions with the copolymer than with the unmodified polymer?

Suggested Extensions

1. Perform the accelerated plasticizer retention test by heating plasticized strips at 150° C and checking loss in weight every hour for 12 hours.
2. Measure tensile strength, Shore hardness, and low-temperature flexibility as a function of plasticizer percentage.
3. Examine other plasticizers, such as dibenzyl and ditetrahydrofurfuryl sebacate.
4. Study the plasticizer content versus the solvent resistance of the composition.
5. Study plasticizer loss versus the boiling point of a series of related plasticizers.

EXPERIMENT 58

STABILIZERS IN POLYVINYL CHLORIDE AND ITS COPOLYMERS

Effect of Lead Compounds on Polyvinyl Chloride Moldings

Plasticize the following lots of polyvinyl chloride polymers in a manner similar to that indicated in Experiment 57.

Sample	*Polymer*	*Plasticizer*	*Stabilizer*
1	Polyvinyl chloride, 60 parts	Tricresyl phosphate, 40 parts	None
2	Polyvinyl chloride, 60 parts	Tricresyl phosphate, 40 parts	Lead amylphenate, 2 parts
3	Polyvinyl chloride, 60 parts	Tricresyl phosphate, 40 parts	Lead oxide, 2 parts
4	Polyvinyl chloride, 60 parts	Tricresyl phosphate, 40 parts	Lead silicate, 2 parts
5	Polyvinyl chloride, 60 parts	Tricresyl phosphate, 40 parts	Lead titanite, 2 parts
6	Polyvinyl chloride-acetate, 60 parts	Tricresyl phosphate, 40 parts	Lead silicate, 2 parts

The lead amylphenate is prepared by adding 1 mole of dry litharge to 2.1 moles of molten amylphenol at 150° C. The additions should be made in small portions, mixing in each portion thoroughly. Continue heating the reaction until all the water is eliminated and until a cooled sample remains clear. Cool the sample, break it into smaller pieces, and powder it with a mortar and pestle. Bottle the sample and keep out of contact with moisture.

Blend the polyvinyl chloride, the tricresyl phosphate, and the stabilizer, if required, in a beaker, and place on milling rolls with front roll heated with 15 to 20 pounds of steam and rear roll maintained cool by running water. Mill for approximately 5 minutes after uniformity is obtained.

Mold three disks of each sample. Save one sample of each lot as a control by storing in a cool dark place. Place one sample of each lot in a 80° C oven and observe at the end of one and two weeks. Expose another sample of each lot to sunlight for 2 to 4 weeks or to the light of a mercury arc light for 48 to 96 hours. Compare the condition of all treated samples with the controls. Record the color changes in the following chart:

	Condition of Samples			
Sample	*Control*	*80° C—1 Week*	*80° C—2 Weeks*	*Sunlight*
1	....	....	....	....
2	....	....	....	....
3	....	....	....	....
4	....	....	....	....
5	....	....	....	....
6	....	....	....	....

QUESTIONS

1. What is the function of the lead phenate? How does it prevent discoloration?
2. What substances other than lead derivatives also act as stabilizers?
3. Discuss the differences in the five lead derivatives tested.
4. What disadvantages would be found in the use of lead tetraethyl and lead tetraphenyl as stabilizers?

EXPERIMENT 59

PREPARATION OF VINYLIDENE CHLORIDE

Before starting this experiment refer to Experiment 54, since the experiments have principle and procedure in common.

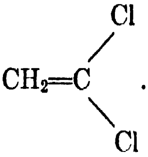
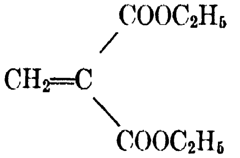
Assemble the apparatus as pictured in Figure 8, using a three-necked flask equipped with a glass stirrer with mercury seal, thermometer, dropping funnel, and reflux condenser. Attached to the top of the reflux condenser is a second condenser set downward for distillation and leading into a flask immersed in an acetone and dry-ice bath. Introduce into the three-necked flask about 350 cc of ethyl alcohol and add 125 grams of C.P. potassium hydroxide pellets. *Regulate the temperature of the water flowing through the reflux condenser to 35 to 40° C* from a suitable source. Water at this temperature may be obtained by running a suitable mixture of hot and cold water into a second flask fitted with a thermometer and feeding this water into the reflux condenser. Use cold water in the other condenser, which serves to liquefy the vinylidene chloride. Then heat the three-necked flask to about 50° C in a steam bath or with an electric heater.

> *Caution.* Do not use a gas flame as vinylidene chloride is highly inflammable and explosive. Make sure the water circulating through the reflux condenser is maintained at 35 to 40° C and that cold water is running through the distillation condenser. Preferably, this experiment should be carried out under a hood.

Place 185 cc of redistilled trichloroethane in the separatory funnel and add it to the reaction flask from the dropping funnel at a rate of about two drops per second. Continue the heating until the temperature of the reaction flask reaches 65 to 75° C and maintain at this temperature, which is just slightly below the boiling point of the ethyl alcohol. Observe the thermometer at the top of the reflux condenser carefully. If the temperature at that point rises above 35° C, it will be necessary to run cold water into the reflux condenser to lower the temperature to 35° C. The formation of vinylidene chloride proceeds readily, but the reflux temperature must be controlled to prevent contamination with other vapors. Stirring at a moderately slow rate is continued throughout the preparation.

For further use, the liquefied vinylidene chloride monomer which has been cooled in the receiving flask is redistilled. Set up a distillation apparatus, using a 2-foot condenser column packed with glass Raschig rings. Redistill the vinylidene chloride without transferring it from the original receiving flask and receive the redistilled vinylidene chloride in a clean flask set in the same dry-ice and acetone bath used for the first part of the experiment. Do not remove the original receiving flask of vinylidene chloride from the dry-ice bath until ready to proceed with the redistillation. Maintain the vinylidene chloride in a refrigerated condition at a temperature below its boiling point until ready for use.

QUESTIONS

1. Compare the chemistry of this experiment with that of Experiment 54 and indicate the relative polymerization rates of (*a*) vinyl chloride, $CH_2{=}CHCl$, and (*b*) vinylidene chloride,  $CH_2{=}C(Cl)_2$. With these results in mind, predict the comparative polymerization rates of ethyl acrylate, $CH_2{=}CHCOOC_2H_5$, and methylene diethyl malonate  $CH_2{=}C(COOC_2H_5)_2$
2. Write the equations for the reactions for the preparation of vinylidene chloride, starting with inorganic materials only.
3. Give the equations for the synthesis of vinylidene iodide, vinylidene bromide, and vinylidene fluoride, and predict the relative rates of polymerization of these monomers.
4. Explain why it is necessary to maintain the temperature of the refluxing condenser at about 35° C.

EXPERIMENT 60

POLYMERS AND COPOLYMERS OF VINYLIDENE CHLORIDE

Part A. Polymerization of Vinylidene Chloride

Use as a reaction chamber a Pyrex glass tube 12 inches long with an inside diameter of about 15 mm, sealed at one end. This tube is graduated to a 20-cc volume to enable the worker to measure out 20 cc of the monomers into the reaction chamber. Refer to the table below, and label the tubes accordingly. In those tubes requiring benzoyl peroxide introduce 0.02 gram of benzoyl peroxide into the tube by means of a long-stemmed funnel to prevent its accumulation on the walls of the tube. Immerse the glass tube in a dry-ice-chloroform-carbon tetrachloride bath in a thermos flask and allow the tube to cool to the temperature of the bath. By means of a long-stemmed funnel introduce the vinylidene chloride directly into the Pyrex reaction chamber while the chamber is immersed in the dry-ice bath. *Protect your eyes with safety goggles and seal the open end of the tube while it is still in the cooling bath.* Remove the tube from the bath and allow it to warm up to room temperature, then polymerize the vinylidene chloride under the conditions expressed in the following table and observe until the polymerization is complete.

Tube	*Benzoyl Peroxide*	*Polymerizing Conditions*	*Polymerization*	*Solubility of Polymer in Methyl Ethyl Ketone*
1	None	Dark	....	....
2	0.02 gram	Dark	....	....
3	None	Ultraviolet light	....	....
4	0.02 gram	Ultraviolet light	....	....
5	None	40° C	....	....
6	0.02 gram	40° C	....	....

The polymerization time means the time of complete polymerization of the monomer, which can be judged by inverting the tube. If no liquid monomer falls to the bottom of the tube, the polymerization may be considered complete.

To remove the polymer, cool the tube in the dry-ice bath, wrap it in a piece of heavy canvas, and crack the glass with a heavy metal object. Separate the polymers from the glass and use the polymer for solubility and molding tests. These samples are to be molded at a temperature of 140 to 150° C at 2000 to 4000 pounds per square inch, and in about 15 minutes. Cool the mold to approximately room temperature before removing the mold sample.

Part B. Tests on Polyvinylidene Chloride

1. Heat a glass rod to a sufficiently high temperature to melt but not char the molded polymer. Touch the hot rod to a corner of the molded polymer and draw out a fiber.

Allow the fiber to cool for a few minutes and then, holding both ends of the fiber, stretch it by applying tension to it very slowly and note if cold drawing occurs. This may be noted by a decrease in the diameter of the fiber and, in many cases, by other visual changes in appearance. A sharp boundary will mark the cold-drawn area, and little or no elastic recovery will occur in the drawn fiber.

2. Hold the corner of the molded piece over the tip of the flame of a Bunsen burner until the polymer melts and catches fire. Remove from the flame and note whether the flame is self-extinguishing.

3. Saw off chips of the molded polymer and insert in test tubes. Test for chemical resistance to the following reagents and record the test results after at least 48 hours of immersion.

Reagents	*Test Results*
Concentrated hydrochloric acid	....
20% sodium hydroxide	....
Concentrated (28%) ammonium hydroxide	....
5% ammonium hydroxide	....

Part C. Copolymers of Vinyl Chloride and Vinylidene Chloride

Refer to Experiment 56 and prepare copolymers of vinyl chloride and vinylidene chloride in 10% steps by the technique of the vinyl chloride experiment, using the proper amount of catalyst, etc. Take the proper safety precautions to avoid fires and explosions.

Label the tubes consecutively according to the table below.

			Polymerization		
Tube	*Parts of Vinylidene Chloride*	*Parts of Vinyl Chloride*	*Time*	*% Yield*	*Solubility in Methyl Ethyl Ketone*
1	10	0	....	....	....
2	9	1	....	....	....
3	8	2	....	....	....
4	7	3	....	....	....
5	6	4	....	....	....
6	5	5	....	....	....
7	4	6	....	....	....
8	3	7	....	....	....
9	2	8	....	....	....
10	1	9	....	....	....
11	0	10	....	....	....

When polymerization is complete, isolate and dry the copolymers, record the yield of polymer in percentage, and save the polymers for use in the following tests:

1. Mold the copolymers at 140 to 150° C for about 15 minutes at 2000 to 4000 pounds per square inch, chilling the mold before removing the molded pieces.

2. Saw up pieces of molded polymer and insert in test tubes. Test the chemical resistance of the polymer to the following reagents and record the test results after at least 48 hours of immersion.

Reagents	*Test Results*
Concentrated hydrochloric acid	....
20% sodium hydroxide	....
Concentrated (28%) ammonium hydroxide	....
5% ammonium hydroxide solution	....

3. Heat a glass rod to a sufficiently high temperature to melt but not char the polymers and copolymers. Touch the hot rod to a corner of each of the molded polymers and draw out a fiber. Allow these fibers to cool for a few minutes. Then, holding both ends of the fiber, stretch it by applying tension to it very slowly and note if cold drawing occurs. This may be noted by a decrease in the diameter of the fiber and in many cases by other visual changes in appearance. A sharp boundary will mark the cold-drawn area and little or no elastic recovery will occur on drawing.

QUESTIONS

1. What is the difference in the methyl ethyl ketone solubility of polyvinyl chloride and polyvinylidene chloride? How does this solubility change with composition in a copolymer of vinyl chloride and vinylidene chloride?
2. Is polyvinylidene chloride an amorphous or crystalline polymer and how is this state affected by its previous history and treatment?
3. How are the cold drawing properties of the vinylidene chloride polymers related to composition in a vinyl chloride copolymer?

Suggested Extension

1. Prepare and study a series of copolymers of vinylidene chloride with other $CH_2{=}C\langle$ compounds, e.g., vinyl acetate, methyl acrylate, and acrylonitrile.

EXPERIMENT 61

PREPARATION AND POLYMERIZATIONS OF POLYALLYL ESTERS

Part A. Preparation of Diallyl Phthalate

In a 500-cc flask equipped with a reflux condenser and a Stark and Dean apparatus (Figure 6) for the continuous removal of water, place 250 cc of benzene or toluene, 74 grams of phthalic anhydride, 87 grams of allyl alcohol, 1.5 grams of toluenesulfonic acid, and 0.5 gram of copper filings. Reflux the mixture until no more water is collected in the Stark and Dean apparatus. Cool the reaction mixture and neutralize the solution with 10% aqueous sodium bicarbonate, using a separatory funnel. Drain the water layer and dry the benzene layer for at least 24 hours over anhydrous sodium sulfate. Filter the solution, remove the benzene or toluene from the diallyl phthalate by distillation at atmospheric pressure, and distill the diallyl ester at a reduced pressure. The boiling point of diallyl phthalate is 175° C at 9 mm or 150° C at 1 mm. Record the percentage yield and actual and theoretical yields in grams. Any polyallyl ester may be made by this procedure. By replacing the phthalic anhydride with another carboxylic acid, for example, adipic, succinic, citric, it is possible to prepare allyl adipate, succinate, citrate, etc.

Part B. Thermosetting Polymers of Diallyl Phthalate

Dissolve 0.5 gram of benzoyl peroxide in 25 grams of diallyl phthalate in a suitable clean glass container. Heat the solution at 65° C. An unpourable gel will form in 16 to 24 hours, after which time the temperature is raised to 70° C for 120 hours. Remove the casting from the glass container, breaking the container if necessary. Test the solubility of a sample of the polymer in benzene, acetone, ethyl alcohol, dioxane, and ethyl acetate. Determine the fusibility of the polymer at 100° C, at 150° C, and at 200° C.

Part C. Partial Polymers of Diallyl Phthalate

1. Mix in a 500-cc flask 30 grams of diallyl phthalate, 150 cc of benzene, and 0.3 gram of benzoyl peroxide, and reflux the mixture for 45 minutes. If the material gels, repeat the experiment, using a shorter time of heating and cool before gelation occurs. Allow the mixture to cool and pour into 500 cc of methyl alcohol, stirring rapidly. Filter the precipitate and dry the powder at room temperature. Save the polymer for further tests in Experiment 62. Record the weight of the dry partial polymer. Test the solubility in benzene, acetone, ethyl alcohol, dioxane, and ethyl acetate. Determine the fusibility of the polymer. Contrast the fusibility of these polymers with those of Part *B* of this experiment.

2. Dissolve a sample of the partial polymer in acetone to produce a 20% solution of polymer in solvent. Add 3% benzoyl peroxide calculated on the weight of the polymer and pour a thin film on glass. Allow the acetone to evaporate at room temperature, then bake the film at 130 to 140° C for 20 to 30 minutes. Remove the film from the glass and test its solubility in acetone.

QUESTIONS

1. Show by using structural formulas why diallyl phthalate should produce insoluble polymers.
2. Indicate a possible structure for a soluble, fusible partial polymer of a diallyl ester.

Suggested Extensions

1. Study the polymerizability of a series of polyallyl esters, e.g., carbonic, oxalic, malonic, and succinic acids of the alpha-omega series, and determine whether separation of the allyl ester groups reduces the polymerization tendency.
2. Study the effect of the addition of monoallyl esters, e.g., allyl benzoate and monoallyl acid phthalate, to the polymerization of a polyallyl ester such as diallyl phthalate or succinate.
3. Study the effect on the polymerization rate of a polyallyl ester when unsaturated alkyd resins are added to the polyallyl ester in the presence and absence of peroxides. The alkyd resins should be of three types: (1) Where the aliphatic unsaturation resides in the dibasic acid, e.g., maleic anhydride with diethylene glycol. (2) Where the aliphatic unsaturation resides in the alcohol or its equivalent, e.g., butadiene monoxide and succinic or phthalic acid. (3) Where the aliphatic unsaturation resides in both the alcohol and the acid, e.g., maleic acid and butadiene oxide.

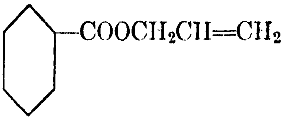
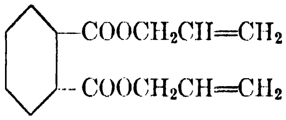
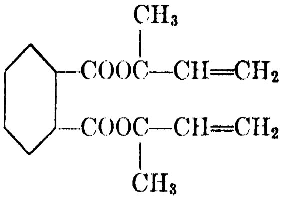
EXPERIMENT 62

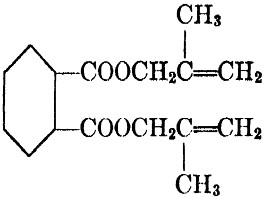
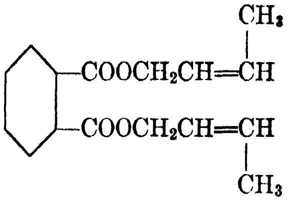
RELATION OF THE ALLYL STRUCTURE TO POLYMERIZABILITY

Part A

In each of a series of six-screw-cap vials place 5 cc of each of the five monomers given in Table I, together with the indicated quantity of benzoyl peroxide, and heat in an oven at 60° C for at least 144 hours. Observe the tendency to polymerize as well as the rate of polymerization. Record the observations in Table I.

TABLE I

Vial	*% Peroxide, Grams*	*Monomer 1* 	*Monomer 2* 	*Monomer 3* 
1	0.1			
2	0.5			
3	1.0			
4	2.0			
5	3.0			
6	4.0			

Vial	*% Peroxide, Grams*	*Monomer 4* 	*Monomer 5* 
1	0.1		
2	0.5		
3	1.0		
4	2.0		
5	3.0		
6	4.0		

These monomer esters are made by using the proper acids and alcohols according to the procedure used for the preparation of diallyl phthalate in Experiment 61*A*. The diallyl phthalate of Experiment 61 may be used in this experiment. For the preparation of the specific ester, the following amounts of acid, alcohol, the toluene sulfonic acid catalyst, 0.59 copper powder, and hydrocarbon (benzene or toluene) are recommended in Table II. Record the boiling points of these esters.

TABLE II

Ester	Acid, Grams	Alcohol, Grams	Catalyst, Grams	Benzene
1. Allyl benzoate	Benzoic, 61	Allyl, 87	1.5	250 cc
2. Diallyl phthalate	Phthalic anhydride, 74	Allyl, 87	1.5	250 cc
3. Di(methyl vinyl carbinyl) phthalate	Phthalic anhydride, 74	Methyl vinyl carbinol, 108	1.5	250 cc
4. Dimethallyl phthalate	Phthalic anhydride, 74	Methyallyl, 108	1.5	250 cc
5. Dicrotyl phthalate	Phthalic anhydride, 74	Crotyl, 108	1.5	250 cc

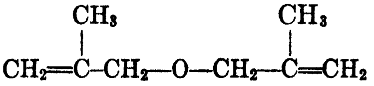
Part B

In the following series of experiments, use sealed combustion tubes instead of glass vials and polymerize the following monomers according to the procedure in Part *A*. Record the observations in Table III.

1. Allyl alcohol
2. Allyl ethyl ether
3. Diallyl ether
4. Dimethallyl ether

TABLE III

		Polymer 1	Polymer 2
Vial	% Peroxide, Grams	$CH_2{=}CHCH_2OH$	$CH_2{=}CHCH_2OCH_2CH_3$
1	0.1		
2	0.5		
3	1.0		
4	2.0		
5	3.0		
6	4.0		

		Polymer 3	Polymer 4
Vial	% Peroxide, Grams	$CH_2{=}CHCH_2OCH_2CH{=}CH_2$	 $CH_2{=}C(CH_3){-}CH_2{-}O{-}CH_2{-}C(CH_3){=}CH_2$
1	0.1		
2	0.5		
3	1.0		
4	2.0		
5	3.0		
6	4.0		

QUESTIONS

1. **Compare the behavior of allyl acetate with vinyl acetate.**
2. **Compare the monoallyl esters with the polyallyl esters.**
3. **Compare the monoallyl ethers with the polyallyl ethers.**
4. **Predict the differences between vinyl ethyl ether and allyl ethyl ether.**

EXPERIMENT 63

COPOLYMERIZATION OF VINYL ACETATE AND DIALLYL DERIVATIVES

Part A. Preparation of Copolymer, Using Monomers

In small screw-cap vials, each containing 0.1 gram of benzoyl peroxide, place the following mixtures of redistilled vinyl acetate and diallyl phthalate, numbering the tubes as indicated:

Tube	*Vinyl Acetate, cc*	*Diallyl Phthalate, cc*
1	10.00	0.00
2	9.99	0.01
3	9.95	0.05
4	9.50	0.50
5	9.10	0.90
6	9.00	1.00
7	8.50	1.50
8	8.00	2.00
9	7.00	3.00
10	6.00	4.00
11	0.00	10.00

Seal the vials and, by shaking, dissolve the benzoyl peroxide in the liquid monomers. Place the vials in an oven at 50° C for 48 hours. Follow this by heating in an oven at 60° C for approximately 48 hours or until the material shows no further change. Continue the cure for another 120 hours at 70° C. A series of castings is obtained, not all of which will be perfect. Those with low diallyl phthalate will bubble since they are not sufficiently cross-linked; those with high diallyl phthalate may be gels instead of solids. Test these castings or portions of them for solubility in solvents such as acetone, glacial acetic acid, and amyl acetate. Test them also for moldability or fusibility by observing their behavior on a hot plate at 140° C.

Part B. Preparation of Copolymer, Using Partial Polymer

In small screw-cap vials containing 0.1 gram of benzoyl peroxide put the stated amount of vinyl acetate. Stir the mixture until all the benzoyl peroxide has dissolved. Then add the stated amount of partial polymer of diallyl phthalate prepared in Experiment 61 and dissolve the partial polymer in the vinyl acetate by stirring. When the solution is complete, polymerize the mixture according to the time and temperature schedule used above for monomeric diallyl phthalate.

Tube	*Vinyl Acetate*	*Partial Polymer of Diallyl Phthalate*
12	7	3
13	6	4
14	5	5

QUESTIONS

1. Compare the results obtained by the use of the partial polymer with those obtained with the monomer of diallyl phthalate.
2. Explain the chemical difference between vinyl acetate and diallyl phthalate.
3. Describe the effect of the diallyl phthalate on the vinyl acetate as it affects the appearance of the casting, the fusibility, the heat resistance, and the solvent susceptibility.
4. Write the structural formula of a portion of polyvinyl acetate; of the copolymer resulting from vinyl acetate and diallyl phthalate.
5. Give two syntheses of allyl alcohol.

Suggested Extension

1. Study cross-linkage efficiency of diallyl phthalate on other monomers, e.g., styrene, methyl methacrylate, and ethyl acrylate.

EXPERIMENT 64

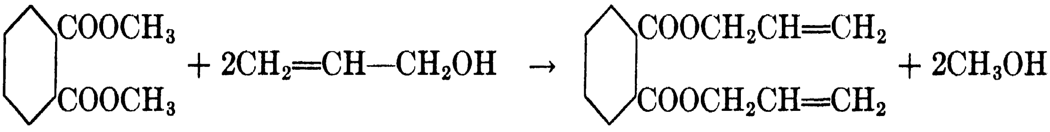
COMPARISON OF ESTER EXCHANGE REACTIONS

Many monomers and even some polymers are prepared by the ester exchange reaction, and the following experiment illustrates side reactions that may be encountered when unsaturated esters are used as starting materials. The ratio of materials indicated below is used for the preparation of two polyallyl esters.

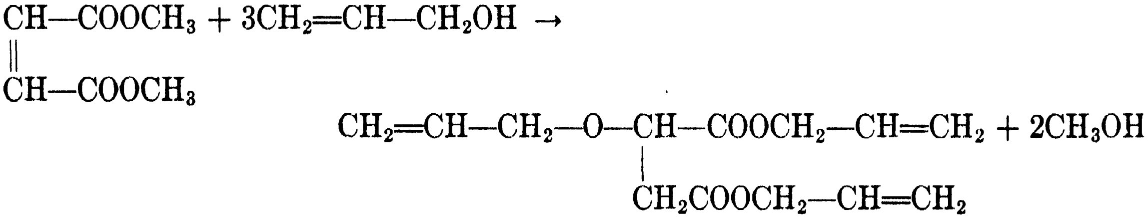
Reaction A		*Reaction B*	
Dimethyl phthalate	194 grams	Dimethyl maleate	144 grams
Allyl alcohol	290 grams	Allyl alcohol	290 grams
Catalyst solution	6 grams	Catalyst solution	6 grams

The difference in the two esterification reactions is shown in the following equations.

Reaction A



Reaction B



$$\begin{array}{l}\mathrm{CH{-}COOCH_3} + \mathrm{3CH_2{=}CH{-}CH_2OH} \rightarrow \\ \| \\ \mathrm{CH{-}COOCH_3}\end{array}$$

$$\begin{array}{l}\mathrm{CH_2{=}CH{-}CH_2{-}O{-}CH{-}COOCH_2{-}CH{=}CH_2} + \mathrm{2CH_3OH} \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad \mathrm{CH_2COOCH_2{-}CH{=}CH_2}\end{array}$$

Part A. Catalyst Preparation

The catalyst is a 2.5% solution of magnesium methylate prepared by dissolving 2.5 grams of clean magnesium ribbon in dry methyl alcohol. The cleansed magnesium, before being dissolved, is activated by being rubbed with mercury. *It is important that the methyl alcohol be dry.*

Part B. Ester Exchange Using Dimethyl Phthalate

The dry dimethyl phthalate, the dry allyl alcohol, and the catalyst are mixed in a 1-liter flask equipped with a thermometer, heating bath, and a reflux condenser. The top outlet of the reflux condenser is connected to a condenser set downward for distillation to collect the methyl alcohol liberated by the reaction. The reflux condenser is maintained at 64 to 66° C, either by water from a thermostatic bath or by a mixture of cold and warm water. This temperature permits the distillation of methyl alcohol and the return to the reaction flask of the other reactants. Start the reaction by maintaining reflux and collect 64 grams of methyl alcohol distillate. The excess allyl alcohol is removed by distillation under reduced pressure and the diallyl phthalate is distilled, boiling at 175° C at 9 mm.

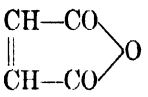
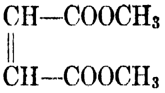
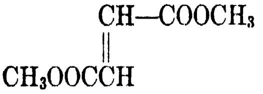
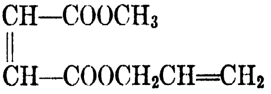
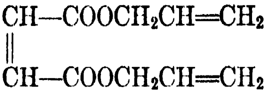
Part C. Ester Exchange Using Dimethyl Maleate

The same procedure is followed as for dimethyl phthalate. The allyloxysuccinate boils at 124 to 136° C at 4 mm. A 90% yield may be expected.

EXPERIMENT 65

POLYMERIZATION OF MALEIC ANHYDRIDE AND ITS DERIVATIVES

In screw-cap vials place the following proportions of reactants, together with 0.2 gram of benzoyl peroxide, and subject the mixture to polymerizing conditions at 60° C for 168 hours. Indicate whether or not the monomers polymerize. Correlate the polymerization tendency of the monomers and the nature of the polymers to the structure of the monomers.

Vial	*Monomer*	*Structure*	*Parts*	*Character of Polymer*
1	Maleic anhydride		10	....
2	Dimethyl maleate or diethyl maleate	 $\begin{array}{l}\text{CH—COOCH}_3\\ \Vert\\ \text{CH—COOCH}_3\end{array}$	10	....
3	Dimethyl fumarate or diethyl fumarate	 $\begin{array}{r}\text{CH—COOCH}_3\\ \Vert\qquad\qquad\\ \text{CH}_3\text{OOCCH}\qquad\end{array}$	10	....
4	Methyl allyl maleate or ethyl allyl maleate	 $\begin{array}{l}\text{CH—COOCH}_3\\ \Vert\\ \text{CH—COOCH}_2\text{CH}{=}\text{CH}_2\end{array}$	10	....
5	Diallyl maleate	 $\begin{array}{l}\text{CH—COOCH}_2\text{CH}{=}\text{CH}_2\\ \Vert\\ \text{CH—COOCH}_2\text{CH}{=}\text{CH}_2\end{array}$	10	....

Some of the above monomers are not commercially available, but they may be prepared in the following manner:

Preparation of Diallyl Maleate

The following materials are mixed in a 1-liter flask equipped with a Stark and Dean apparatus with a reflux condenser:

Maleic anhydride	98	grams
Allyl alcohol	174	cc
Benzene or toluene	500	cc
Toluenesulfonic acid	2.75	grams
Copper wire	1.00	gram

The mixture is reacted until all the water of esterification is eliminated. The reaction mixture is cooled and neutralized in a separatory funnel with 10% aqueous $NaHCO_3$. Separate the water layer, wash with an equal volume of distilled water, separate the water layer, and dry overnight over anhydrous Na_2SO_4. Transfer the dried mixture of benzene, allyl alcohol, and diallyl maleate to a distilling flask containing 1 gram of copper wire or powder. Remove the allyl alcohol and benzene by distillation at atmospheric pressure. The diallyl maleate is distilled at reduced pressure, b.p. 131 to 135° C at 12 mm. The yield is approximately 180 grams.

Preparation of Dimethyl Fumarate

To 20 grams of dimethyl maleate add 2 grams of concentrated HCl and, with stirring, warm to 70° C for 5 minutes in a water bath. Remove from the water bath and let the product stand at least 2 hours. Recrystallize the crystalline dimethyl fumarate from a mixture of equal parts of benzene and methyl alcohol, m.p. 99 to 101° C.

Preparation of Methyl Allyl Maleate

In a three-necked flask equipped with a stirrer, thermometer, dropping funnel, and reflux condenser introduce 98 grams of maleic anhydride and 58 grams of allyl alcohol. Heat the mixture for one hour in a bath at 100° C. Cool to room temperature and add slowly 600 cc of methyl alcohol, in which 56.5 grams of KOH have been dissolved. Reheat the solution to reflux on a water bath and add slowly by dropping funnel 126 grams of dimethyl sulfate. After the addition of the dimethyl sulfate, reflux for one hour. Cool, remove the precipitate by filtration, and distill the filtrate at atmospheric pressure to remove methyl alcohol. Distill the methyl allyl maleate under reduced pressure, b.p. 120 to 126° C at 14 mm.

QUESTIONS

1. Is maleic anhydride or its simple esters polymerized readily?
2. Discuss the polymerizability of the five monomers of this experiment with particular reference to their structures.

EXPERIMENT 66

COPOLYMERS OF MALEIC ANHYDRIDE, ITS DERIVATIVES AND ISOMERS

Part A. Preparation of Copolymers

In screw-cap vials place the compositions indicated below and polymerize them at 75° C for 144 to 168 hours. Record the character of the polymers and their solubilities in acetone.

GROUP I

Vial	*Monomer A*	*Monomer B*		*Benzoyl Peroxide*	*Character of Polymer and Solubility in*	
					Acetone	*Benzene*
1	Styrene 5.2	Maleic anhydride	4.9	0.0	....	....
2	Styrene 5.2	Maleic anhydride	4.9	0.5	....	....
3	Styrene 5.2	Chlormaleic anhydride	6.1	0.5	....	....
4	Styrene 5.2	Maleic acid	5.8	0.5	....	....
5	Styrene 5.2	Fumaric acid	5.8	0.5	....	....

GROUP II

Vial	*Monomer A*	*Monomer B*		*Benzoyl Peroxide*	*Character of Polymer and Solubility in*	
					Acetone	*Benzene*
6	Styrene 5.2	Dimethyl maleate *	7.2	0.1	....	....
7	Styrene 5.2	Dimethyl maleate *	2.4	0.1	....	....
8	Styrene 5.2	Dimethyl fumarate *	2.4	0.1	....	....
9	Styrene 5.2	Methyl ethyl maleate	8.4	0.15	....	....
10	Styrene 5.2	Diallyl maleate	9.8	0.15	....	....

* The diethyl esters may be used in place of the dimethyl esters.

Part B. Laboratory Preparation of Styrene-Maleic Anhydride Copolymer

In a 500-cc three-necked flask equipped with stirrer, thermometer, reflux condenser, and a heating bath introduce the following ingredients:

Benzene or toluene	300 cc
Maleic anhydride	10.4 grams
Styrene	9.8 grams
Benzoyl peroxide	0.1 gram

Stir at room temperature until solution is accomplished. Heat the bath to 70° C until the temperature of the reaction mixture becomes 70° C. When the temperature of the reaction mass begins to drop, renew the heating *slowly*, bringing the reaction to reflux. Maintain reflux for one hour, then cool the reaction product while maintaining stirring. Suction-filter the solid copolymer and dry first overnight at room temperature under a hood by spreading the polymer on a filter paper to remove the bulk of the hydrocarbon solvent. The product is further dried in a 70° C oven to constant weight. Record the yield in percentage of the theoretical if the assumption is made that one mole of styrene reacts with one mole of maleic anhydride. Determine the melting point of the product.

Part C. Reactions of Styrene-Maleic Anhydride Copolymer

1. Dissolve 5 grams of copolymer in 50 cc of acetone and pour with "vigorous stirring" into 150 cc of water. Filter off the precipitate, dry as for styrene-maleic anhydride copolymer, and determine melting point of the product. Write the chemical reaction for the reaction of the maleic anhydride copolymer with water.
2. Add 5 grams of copolymer to 50 cc of ethyl alcohol and 0.05 gram of toluenesulfonic acid and reflux for 10 minutes. Pour the mixture into 150 cc of water with vigorous stirring, filter off the precipitate, dry, and record the melting point of the product. Write the equation for the reaction of the copolymer with ethyl alcohol to give the acid ester.
3. Add 5 grams of the copolymer in 100 cc of water containing 1 gram of sodium hydroxide. Note if solution occurs and if the product possesses any of the properties of a wetting agent. Write the equation for the reaction.

QUESTIONS

1. Compare the copolymerizability of the monomers in Group I with their structure and solubility. Why was fumaric anhydride omitted from the list of monomers?
2. Contrast the esters in Group II with the anhydrides and acids of Group I.
3. Contrast the copolymerization of the esters of Group II among themselves with particular reference to structure, functionality. How is the insolubility of the copolymer affected by the functionality of the ester? Does the fumaric ester copolymerize faster than the maleic ester?
4. Write the equations for the reaction of one mole of styrene with one mole of maleic anhydride. Give the equations for the reaction of the copolymer with water, ethyl alcohol, sodium hydroxide, and ethylene glycol.

Suggested Extensions

1. Prepare a series of copolymers of styrene and maleic anhydride in benzene solution or in another solvent which causes precipitation of the copolymer, vary the mole ratio of styrene to maleic anhydride from a large molar excess of styrene on one end to a large molar excess of maleic anhydride on the other, and determine the composition of the precipitated copolymer as compared with the composition of the starting monomer mixture.
2. The results of Suggested Extension 1 should be compared with a non-precipitant solvent such as acetone and with mass castings in the absence of any added solvent.
3. Use other $CH_2{=}C\langle$ compounds such as the acrylic and methacrylic ester and corresponding nitriles, vinyl acetate, and the chlorinated styrene monomers with maleic anhydride and related derivatives.
4. Study the polymerizability and copolymerizability of maleic derivatives of the type as maleic imide, N-substituted maleic imides, maleic and fumaryl nitriles, amides, etc., and determine the effects on a copolymer with respect to heat and solvent resistance.

EXPERIMENT 67

DEPOLYMERIZATION OF POLYMERS

Part A. Depolymerization of Methyl Methacrylate Polymer

Set up a vacuum distillation apparatus using an efficient condenser, and in the distilling flask place 20 to 30 grams of finely ground polymeric methyl methacrylate. The receiver is attached to a vacuum system of 0.5 to 2 mm through a series of two traps cooled with dry-ice acetone cooling mixture. Heat the distilling flask by means of a suitable sand or metal alloy bath to 300 to 400° C, and collect the distillate under reduced pressure for a period of 5 to 6 hours. The distillate is purified by distillation at atmospheric pressure in a suitable distilling apparatus containing about 0.5% of hydroquinone in the distilling flask as a polymerization retarder. Collect the fraction boiling between 96 and 104° C (b.p. pure methyl methacrylate, 100° C) and identify it by means of boiling point, refractive index, and specific gravity. Record the results below.

	Methyl Methacrylate	
	Depolymerized Product	*Pure Known Monomer*
Boiling point	....	....
Refractive index	....	....
Specific gravity	....	....
% Yield of monomer	....	

If a commercial sample of polymer is used and if it is a copolymer, wider boiling fractions will be obtained and further fractionation may be required.

Part B. Depolymerization of Styrene

In the same equipment as used in Part *A* introduce 20 to 30 grams of polystyrene and degrade as for methyl methacrylate. Collect the distillate as above and refractionate in the presence of 0.5% sulfur as inhibitor, isolating a monomer and dimer fraction. Use the monomer fraction for further comparative test.

	Boiling Point	*% Yield*
Monomer	143 °C	....
Dimers	310 to 312° C	....
Residual trimers, etc.	>312° C	....

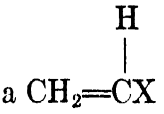
	Styrene	
	Depolymerized	*Monomer*
Boiling point	....	....
Refractive index	....	....
Specific gravity	....	....
% Yield of monomer	....	

QUESTION

1. Compare the yield of methyl methacrylate monomer to styrene monomer. From the structure of the polymers present an explanation for the differences in yields.

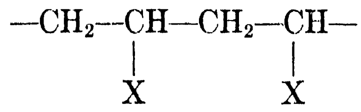
EXPERIMENT 68

DETERMINATION OF POLYMER STRUCTURE



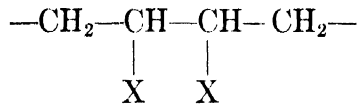
The polymerization of a $CH_2{=}\overset{H}{\overset{|}{C}}X$ compound offers a means of determining whether the polymerization has occurred in one of the following ways.

Structure 1 Head-to-tail



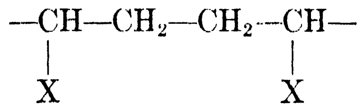
$$-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-$$

Structure 2 Tail-to-tail



$$-CH_2-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-CH_2-$$

Structure 3 Head-to-head



$$-\underset{X}{\underset{|}{CH}}-CH_2-CH_2-\underset{X}{\underset{|}{CH}}-$$

It is to be noted that if structures 2 and 3 are continued in space, they become equivalent in structure. Polymers of the esters of α-haloacrylic acid are well adapted to a simplified laboratory demonstration of how such a problem may be attacked since they contain reactive halogen groups.

Part A. Preparation of the Polymeric Methyl α-Bromoacrylate

Refer to Experiment 48, and using bromine instead of chlorine, prepare methyl α,β-dibromopropionate and dehydrohalogenate this ester by treating one mole of ester with one mole of quinoline to obtain the methyl α-bromoacrylate. The yield is approximately 80 to 85%, the boiling point is 72.5 to 74° C at 78 mm, d_{20}^{20} is 1.6, and n_D^{20} is 1.4840. Polymerize the distilled ester as follows:

Dissolve 10 parts of methyl α-bromoacrylate in 50 cc of dry dioxane, add 0.25 gram of benzoyl peroxide, and place in an oven at 35° C for 48 hours before adding 0.25 gram more of benzoyl peroxide. Heat again for 48 hours. Precipitate the polymer by the addition of 250 cc of ether, filter the polymer, and rewash the polymer with ether, and dry. Record the yield of polymer in ______ grams.

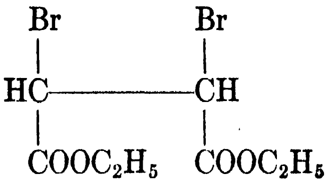
Part B. Determination of Structure

Dissolve 1.66 grams of polymeric methyl α-bromoacrylate in 88 grams of peroxide-free dioxane. Add an acetone solution of KI in sufficient quantity to contain at least 3 moles of KI per each mole (166 grams) of polymeric α-bromoacrylate re-occurring unit. Heat the mixture for 24 to 72 hours at 100° C, and test a sample of the solution for the liberation of I_2 by use of a starch indicator. If time permits, titrate the liberated iodine, if any, with standard thiosulfate solution for the percentage of conversion.

Part C. Interpretation of the Reactions

The liberation of iodine from KI has been studied with compounds having multiple halogens. Compounds of the following type have been studied.

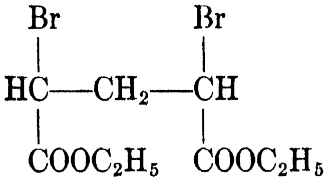
1. Ethyl α-α'-dibromosuccinate of the formula



$$\mathrm{HC(Br)(COOC_2H_5){-}CH(Br)(COOC_2H_5)}$$

which corresponds to a tail-to-tail structure:

2. Ethyl α,α'-dibromoglutarate of the formula



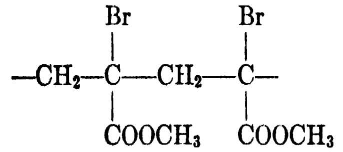
$$\mathrm{HC(Br)(COOC_2H_5){-}CH_2{-}CH(Br)(COOC_2H_5)}$$

which corresponds to a head-to-tail structure, No. 1.

Experimental results show that for all practical purposes the glutarate does not liberate iodine from KI whereas the succinate does.

QUESTION

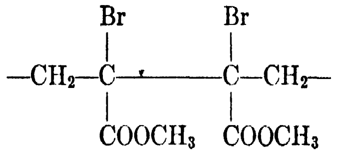
1. From the results of your tests indicate which structure is the structure for your polymer—



$$\mathrm{{-}CH_2{-}C(Br)(COOCH_3){-}CH_2{-}C(Br)(COOCH_3){-}}$$

Structure 1

or



$$\mathrm{{-}CH_2{-}C(Br)(COOCH_3){-}C(Br)(COOCH_3){-}CH_2{-}}$$

Structure 2

PROOF OF COPOLYMERIZATION OF ACRYLIC TYPE—COLD DRAWING

Part A. Preparation of Polymers

In sealed tubes cast the polymers and copolymers listed below, using 0.25% benzoyl peroxide at 40° C for 4 hours, at 50° C for 4 hours, at 60° C for 8 hours, and at 70° C for 1 week.

Sample	*Acrylonitrile, Grams*	*Ethyl Acrylate, Grams*	*Description of Polymer*	*Solubility*	
				Nitromethane	*Ethyl Acetate*
I	100	0	....	....	....
II	75	25	....	....	....
III	50	50	....	....	....
IV	25	75	....	....	....
V	0	100	....	....	....

Part B. Polymer Compatibility

On milling rolls, using one roll heated by 20 pounds of steam and the other roll maintained cool by running water, process the following mixtures in the ratios given and note whether they are compatible. If homogeneity is not accomplished in 5 minutes of milling, record the mixture as incompatible.

Sample	*Resin of Sample I (Polyacrylonitrile)*	*Resin of Sample V (Polyethyl Acrylate)*	*Compatibility*
VI	75	25	....
VII	50	50	....
VIII	25	75	....

Mold these samples and compare at least one property of sample II with a similar property of VI, of sample III with VII, and of sample IV with VIII, and record in the table below.

	Samples					
	II 75 : 25 *Copoly.*	VI 75 : 25 *Mix.*	III 50 : 50 *Copoly.*	VII 50 : 50 *Mix.*	IV 25 : 75 *Copoly.*	VIII 25 : 75 *Mix.*
Composition	....	....	....	....	....	....
Appearance	....	....	....	....	....	....
Impact strength	....	....	....	....	....	....
Flexural strength	....	....	....	....	....	....
Solubility in ethyl acetate	....	....	....	....	....	....
Solubility in nitromethane	....	....	....	....	....	....

Part C. Cold Drawing as Proof of Copolymerization

Prepare a 3% solution in nitromethane of samples II, III, IV, and V. Sample I does not dissolve. Pour films of these solutions on glass plates and allow them to air-dry for 24 hours before drying the films in an oven at 65 to 70° C for at least 8 hours. Strip off the films from the glass, immersing the glass and films in water for a short while, if necessary, to peel off the film. Cut thin ribbons from the stripped film and test for cold-drawing properties. The procedure of cold drawing and the characteristic of a cold-drawn polymer are indicated in Experiment 60. Further evidence of cold drawing may be noted under crossed Polaroid sheets.

EXPERIMENT 70

PROOF OF COPOLYMERIZATION OF VINYL TYPE

Follow the general principle outlined in Experiment 69, and by milling on rolls compound commercial samples of polyvinyl chloride and polyvinyl acetate in the same ratio as found in three commercial copolymers of vinyl chloride and vinyl acetate of known composition. Use ethyl acetate and ethylene dichloride in the solvent tests.

Plan and execute a series of experiments proving that the copolymer is a copolymer and not a mixture of resins.

Part A. Examination of Known Copolymers

	Composition of Copolymer		*Description of Copolymer*	*Solvent A*	*Solvent B*
	Vinyl Chloride	*Vinyl Acetate*			
Sample I	100	0	....	....	....
Sample II	...	...	....	....	....
Sample III	...	...	....	....	....
Sample IV	...	...	....	....	....
Sample V	0	100	....	....	....

Part B. Mixtures of Polyvinyl Chloride and Polyvinyl Acetate

	Composition of Mixture		*Compatibility*
	Polyvinyl Chloride	*Polyvinyl Acetate*	
Sample VI	....	....	....
Sample VII	....	....	....
Sample VIII	....	....	....

Part C. Comparison of Known Copolymers and Mixtures of Polymers

Sample number	II	VI	III	VII	IV	VIII
	Copoly.	*Mix.*	*Copoly.*	*Mix.*	*Copoly.*	*Mix.*
Composition	....	....	....	....	....	....
Appearance	....	....	....	....	....	....
Impact strength	....	....	....	....	....	....
Flexural strength	....	....	....	....	....	....
Solubility solvent *A*	....	....	....	....	....	....
Solubility solvent *B*	....	....	....	....	....	....

QUESTION

1. Using the data in Part *C*, interpret the results to show that the commercial product is a true copolymer and not a physical mixture of polyvinyl chloride and polyvinyl acetate.

EXPERIMENT 71

PROPERTIES VERSUS CONSTITUTION—ACRYLONITRILE AND METHACRYLONITRILE

Acrylonitrile versus Methacrylonitrile

Part A. Solubilities. Test the solubility of monomeric acrylic nitrile and methacrylic nitrile in acetone, acetic acid, ethyl alcohol, acetic anhydride, nitromethane, and nitroethane.

Part B. Polymer Solubilities. Prepare a 10-gram mass casting of acrylonitrile and methacrylonitrile, using 0.2% benzoyl peroxide and heating at 70° C until no further visual change is noted in either polymer. Make the following observations and tests on the polymers. If the polymerization at 70° C is too violent, repeat the experiment, allowing the monomers to stand for 4 hours at room temperature, then 24 hours at 50° C, and at 70° C for as long as necessary. Record data in the following table:

	Monomer Acrylonitrile	*Polyacrylonitrile*	*Monomer Methacrylonitrile*	*Polymethacrylonitrile*
Appearance	....	....	....	....
Melting point	....	....	....	....
Boiling point	....		....	
Moldability at 120° C		....		....
Solubility in acetone	....	....	....	....
Solubility in acetic acid	....	....	....	....
Solubility in acetic anhydride	....	....	....	....
Solubility in nitromethane	....	....	....	....
Solubility in nitroethane	....	....	....	....
Solubility in acrylonitrile		....	....	....
Solubility in methacrylonitrile	....	....		....

QUESTIONS

1. Explain the differences in the two polymers. Is the polymer of acrylonitrile of higher molecular weight than that of methacrylonitrile?
2. Contrast the results of this experiment with the differences between methyl (or ethyl) acrylate and methyl (or ethyl) methacrylate.

EXPERIMENT 72

MUTUAL INHIBITION BY MONOMERS

Part A

Prepare, in suitable screw-cap vials, the following mixtures of freshly distilled inhibitor-free monomers, and add 0.5% and 1.0% benzoyl peroxide to these mixtures. Place in an oven at 70° C for one week. Observe at the end of 24 hours and at the end of one week, and record the data below.

			Observations, % Peroxide			
Tube	*Styrene, Grams*	*Vinyl Acetate, Grams*	*0.5 24 Hours*	*1.0 24 Hours*	*0.5 1 Week*	*1.0 1 Week*
1	10	0	....	....	....	....
2	8	2	....	....	....	....
3	6	4	....	....	....	....
4	4	6	....	....	....	....
5	2	8	....	....	....	....
6	1	9	....	....	....	....
7	0	10	....	....	....	....

Part B

Repeat Part *A*, using acrylonitrile in place of styrene.

			Observations, % Peroxide			
Tube	*Acrylo-nitrile, Grams*	*Vinyl Acetate, Grams*	*0.5 24 Hours*	*1.0 24 Hours*	*0.5 1 Week*	*1.0 1 Week*
1	10	0	....	....	....	....
2	8	2	....	....	....	....
3	6	4	....	....	....	....
4	4	6	....	....	....	....
5	2	8	....	....	....	....
6	1	9	....	....	....	....
7	0	10	....	....	....	....

Suggested Extension

1. **Repeat the above experiments, using the same composition of monomers and catalyst but using emulsion or "pearl" polymerization, and determine their copolymerizability and lack of inhibiting influence.**

EXPERIMENT 73

PREPARATION OF BUTADIENE POLYMERIZATES

Prepare about 200 to 250 cc of a 5% sodium oleate solution in distilled water. Place 50 cc of this solution in each of three pressure "citrate" bottles, labeled *A*, *B*, and *C*. Into each bottle place 0.1 gram of dodecylmercaptan. Add 0.25 gram of potassium persulfate to each bottle, and shake until the polymerization catalyst is in solution. Seal bottle *A*. To bottle *B* add 7.5 grams of inhibitor-free styrene, and seal the bottle. To bottle *C* add 7.5 grams of freshly distilled acrylonitrile, and seal the bottle. *Do not shake these bottles.* Place the three bottles in a refrigerator for at least 4 hours, or preferably overnight, before adding liquefied butadiene.

Under a hood, in the absence of all flames and directly from a cylinder of butadiene, and by just cracking the valve, lead gaseous butadiene through a glass tube into an Erlenmeyer flask thoroughly cooled by a dry-ice and alcohol mixture until about 100 cc of liquid butadiene is collected. Leave the flask in the cooling mixture until ready for use.

Caution. Remember to wear goggles at all times since explosions may occur.

Part A. Butadiene Rubber

Remove bottle *A* from the refrigerator, open the bottle, and tare on a balance. Put on the safety goggles and leave them on throughout the remainder of this experiment. Adjust the weights on the balance to 25 grams above the weight of the tare. Now pour in liquid butadiene until the beam of the balance is just tipped. Allow the excess of butadiene to evaporate until the balance indicates 25 grams on the zero point. Seal the bottle, note final weight, and place to one side.

Part B. Butadiene-Styrene Rubber

Using bottle *B*, and repeating the technique of Part *A*, introduce 17.5 grams of butadiene.

Part C. Butadiene-Acrylonitrile Rubber

Using bottle *C*, and repeating the technique of Part *A*, introduce 17.5 grams of butadiene.

Part D. Polymerization of the Butadiene Mixtures

Place the three pressure bottles in a safe place, and allow them to come to room temperature. Shake the bottles vigorously to produce an emulsion, and place them in a thermostated 50° C bath equipped with a continuous shaking or tumbling rack, if available. Start the shaking apparatus and operate throughout the experiment. If shaking equipment is not available, wear goggles and shake the bottles again at the end of one hour. Leave undisturbed for 18 hours. At the end of that time, remove the bottles from the bath and allow them to cool to room temperature; then place them in the refrigerator for one hour. Weigh each bottle to determine if any butadiene has been lost through leakage. Open the pressure bottles cautiously, and pour the latex into a 500-cc beaker. Bottle *A*, which contains only butadiene, may still have a considerable quantity of unpolymerized butadiene and caution should be taken in opening it. Also, considerable foaming due to escaping butadiene may be noted in this and other bottles when they are opened. Stirring vigorously, add to each beaker 0.5 gram of *N*-phenyl-β-naphthylamine. Precipitate the resulting latex by the slow addition of a solution containing 5% of sodium chloride and 2% of sulfuric acid. Add 5 cc of precipitating solution per addition until the precipitation occurs. Using a Büchner funnel, filter the precipitate by suction. With vigorous stirring, wash the precipitate four times with 100 cc of distilled water per washing. Filter, and dry the precipitate at 65 to 70° C. Weigh the yield of the polymer, and report the data in the following table:

	Monomers		*Yield*		*Appearance of*	
	Weight, Grams	*% Ratio*	*Grams*	*%*	*Latex*	*Final Product*
Rubber *A*						
Butadiene	25	100	......	......	....	....
Rubber *B*						
Butadiene	17.5	70	......	......	....	....
Styrene	7.5	30	......	......	....	....
Rubber *C*						
Butadiene	17.5	70	......	......	....	....
Acrylonitrile	7.5	30	......	......	....	....

QUESTIONS

1. Describe qualitatively the properties of the three polymers. What is the effect of styrene and nitrile on the butadiene polymerization rate?
2. What is Buna S? Buna N?
3. Since, chemically, butadiene is divinyl and has two $CH_2{=}CH$— groups, why are these polymers thermoplastic in nature? Are they heat-convertible? Why? Give the most probable chemical structure of the three polymers.
4. What is meant by the 1.4 addition in reference to the dienes? Give at least two examples. Discuss the possibility of a Diels-Alder reaction occurring in some of the above reactions.
5. What is the function of each component used in the preparation of each of the three rubbers?

Suggested Extensions

1. Compare sodium perborate, ammonium persulfate, benzoyl peroxide with potassium persulfate, both in the presence and absence of iron, nickel, stainless steel, copper, etc.
2. Compare a mass to an emulsion polymerization.

EXPERIMENT 74

VULCANIZATION OF BUTADIENE POLYMERIZATES

Compare the three butadiene polymerizates of the previous experiment with natural rubber for some of its properties, using the ratios of ingredients indicated in the formula below.

Rubber or polymer	100 parts
Channel black	50 parts
Zinc oxide	2 parts
Stearic acid	1 part
Sulfur	4 parts
Mercaptobenzothiazole	1 part

For milling practice, consult A.S.T.M. Method D15–41. Maintain the mill temperature at 20 to 40° C, and follow the general procedure suggested below.

Tighten the mill rolls and subject the rubber to two tight refinings. Adjust the mill rolls to give a continuous sheet of rubber, and mill for 10 minutes, making eight to ten three-fourth cuts each way. During the next 10 minutes add the channel black slowly, making four three-fourth cuts during the process. Add the zinc oxide, the stearic acid, the accelerator, and the sulfur during the next minute before making four three-fourth cuts each way. Roll and pass the stock endwise five or six times, sheet out the compound, and allow to stand for about 8 hours. Pass again through tightened rolls, sheet to thickness (see A.S.T.M. D15–41), and mold. Mold samples for 50 minutes at 292° F, using standard A.S.T.M. mold.

Test for tensile strength, elongation, and stress at 300% elongation, according to A.S.T.M. Methods D412–41, sections 6, 7, and 8, and D15–41. Report the results obtained and record the data in the table below. Compare the solvent resistance of the rubbers by immersion in (*a*) gasoline, (*b*) oil, and (*c*) water for 48 hours.

	Rubber A	*Rubber B*	*Rubber C*	*Natural Rubber*
Stress at 300% elongation	....	....	....	....
Tensile strength	....	....	....	....
Elongation at break	....	....	....	....
Gasoline resistance	....	....	....	....
Oil resistance	....	....	....	....
Water adsorption	....	....	....	....

QUESTIONS

1. What is vulcanization?
2. What is the purpose of each of the constituents in the vulcanization formula?
3. Discuss the properties of the synthetic rubber in contrast to natural rubber, and describe the effect of styrene and acrylonitrile as they affect the butadiene in the final properties.

Suggested Extensions

1. Study the effect of varying percentages of channel black on the elongation and other physical properties of the vulcanized copolymers, in contrast to natural rubber.
2. Study the properties of the vulcanized compounded rubber as a function of channel black content.
3. Study the vulcanizability of a butadiene copolymer as the butadiene content is changed.
4. Study the butadiene copolymerizates with other $CH_2{=}C\langle$ compounds, for example, with ethyl acrylate, isobutylene, etc. Of particular interest are those copolymers containing small quantities of butadiene, e.g., butyl rubber, in which the major portion is isobutylene and the minor portion is butadiene or isoprene.

EXPERIMENT 75

COMPARISON OF PLASTIC AND ELASTIC PROPERTIES

Part A

Consult Experiments 73 and 74 on butadiene polymerizates and, following the necessary precautions, particularly as to the use of goggles, prepare a series of polymers of the following relative compositions. Select suitable tests that will distinguish the elastic and plastic properties of these compositions.

> *Caution.* Because the compositions containing more than 60% butadiene may contain considerable quantities of unpolymerized butadiene the polymerization flask should be thoroughly cooled before opening. In these same compositions excessive foaming will be encountered.

Styrene	*Butadiene*	*Yield of Polymer*	*Stability of Latex*	*Appearance of Polymer*
100	0	....	....	....
80	20	....	....	....
60	40	....	....	....
50	50	....	....	....
40	60	....	....	....
30	70	....	....	....
20	80	....	....	....
10	90	....	....	....
0	100	....	....	....

Plot the physical properties, such as the tensile strength, elongation, water resistance, oil resistance, and elasticity, versus the percentage of styrene in the copolymer before and after compounding and vulcanization. The channel black and the other components as well as milling time, etc., must be kept constant to obtain a satisfactory relation of properties to composition.

Part B

Repeat Part *A*, using acrylonitrile instead of styrene. Compare the properties of these copolymers with those in Part *A*.

QUESTIONS

1. Using a constant polymerization time, how is the yield of rubber affected by the amount of styrene or acrylonitrile present?
2. Does the same percentage of acrylonitrile produce a harder and less elastic compound than styrene?
3. How do the rubber and elastic properties change as a function of butadiene concentration?

EXPERIMENT 76

PREPARATION OF POLYALKYLENE SULFIDE

In a three-necked 1-liter flask equipped with stirrer, reflux condenser, thermometer, and dropping funnel put 435 grams of 40% solution of sodium tetrasulfide and 7 grams of magnesium chloride dissolved in 10 cc of water. Heat the contents of the flask to 75 to 78° C and, dropwise, add slowly 79 grams of ethylene dichloride at about 30 drops per minute. Continue refluxing the reaction for about 5 hours after the addition of the ethylene dichloride. Let the reaction mixture cool, and adjust the mixture to a *p*H of 4 to 6 with 5% dilute acetic acid. Let the solid reaction product settle to the bottom of the flask, decant the aqueous layer, agitate, and wash the product with four portions of 500 cc of distilled water. Filter the reaction product and dry in an oven at 50° C, using a vacuum oven if one is available. The dried product is densified on a rubber mill to obtain a tough somewhat elastic composition. The product may be molded at 110° C in a disk or bar mold for 5 minutes. Cool the mold to at least 40° C before removing the molded piece from the mold.

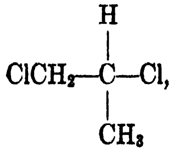
QUESTIONS

1. What class of compounds are responsible for the odor found in polyalkylene sulfide resins? What is the formula of dithiuram?
2. What is the purpose of the magnesium chloride?
3. Predict the differences in rates of condensation of ethylene di-iodide, dibromide, and dichloride with sodium tetrasulfide.
4. How is sodium tetrasulfide prepared?

Suggested Extensions

1. Study the vulcanization of the polyalkylene sulfides, using sulfur alone and in the presence of (*a*) magnesium oxide and (*b*) mercaptobenzothiazole.
2. Study the condensation of a related series of dihalides while maintaining the composition of the polysulfide $Na_2S—S_x$ constant, e.g.,

(*a*) $ClCH_2CH_2Cl$,

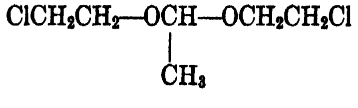


$ClCH_2—\overset{H}{\underset{CH_3}{C}}—Cl$,

$ClCH_2CH_2CH_2Cl$, $ClCH_2CH_2CH_2CH_2Cl$

(*b*) $ClCH_2CH_2Cl$, $ClCH_2CH_2OCH_2CH_2Cl$, $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$

(*c*) $ClCH_2CH_2OCH_2CH_2Cl$, $ClCH_2CH_2OCH_2OCH_2CH_2Cl$,



$ClCH_2CH_2—O\underset{CH_3}{CH}—OCH_2CH_2Cl$

3. Maintain the dihalide constant and study the type of condensation product obtained as the amount of sulfur in the sodium polysulfide is varied, e.g., Na_2S, $Na_2S—S$, $Na_2S—S_2$, $Na_2S—S_{2.5}$, $Na_2S—S_3$.
4. Vary the mole ratio of the dihalide to the sulfide and determine the effect on the chain length of the polymer.

EXPERIMENT 77

PREPARATION OF NITROCELLULOSE

Add slowly, and with care, 35 cc of concentrated H_2SO_4 to 25 cc of concentrated HNO_3 in a 150- to 200-cc beaker. Adjust the temperature of the mixed acids to 35° C by means of a cooling bath. After wrinkling and crushing six sheets of filter paper until they are quite soft, tear the sheets into small bits, and collect 5 grams of the torn paper. Add these pieces of paper, a few at a time, to the mixed acid, and immediately sink them below the surface of the acid with a thermometer, noting the temperature of the mixed acids as the paper is added. Maintain the temperature of acid at lower than 35° C, using a cooling bath if necessary. After the nitrating mixture has stood for one hour, the mixed acids are decanted into 500 cc of water, and then flushed down the sink. The beaker containing the nitrocellulose is rapidly filled with tap water and the entire contents are poured into a 4-liter beaker containing about 3 liters of water. Wash the nitrocellulose with water several times by decantation, and finally suspend the nitrocellulose in ethyl alcohol. Repeat the washing with alcohol at least four times, after which the nitrocellulose is sucked dry on a Büchner funnel.

Test the solubility of the nitrocellulose in alcohol, acetone, ether, amyl acetate, and in a 40 : 60 ether-alcohol mixture. Evaporate a portion of each solution formed on a watch glass. Dry a very small portion of the alcohol-dampened nitrocellulose in a warm room. Test it cautiously for inflammability by igniting it under a hood.

Place the remainder of the damp nitrocellulose in a small mortar, together with 30 to 40% of its weight of camphor. Knead the mixture until the fibrous nature of the nitrocellulose has vanished and a homogeneous plastic mass has resulted. Press the mass into a sheet or block and season in a drying oven at 35 to 40° C.

QUESTIONS

1. Who was the first person to prepare a camphorated nitrocellulose?
2. What are the main advantages and disadvantages of this plastic material?
3. What is the nitrogen content of the cellulose nitrates used in (*a*) explosives, (*b*) coating compositions, (*c*) plastic?
4. What is low-viscosity nitrocellulose, and what is its major use?

EXPERIMENT 78

PREPARATION OF CELLULOSE ACETATES

Part A. The Acetylization Reaction

Dissolve 10 grams of anhydrous zinc chloride in a 250-cc beaker containing 40 cc of glacial acetic acid. Add 5 grams of absorbent cotton to the solution in the beaker, using very small portions of cotton per addition. After each addition, sink the cotton into the solution with a thermometer until all the cotton fibers are saturated before adding more cotton. When all the cotton has been added, let the mixture stand for about 10 to 15 minutes and then add 40 cc of acetic anhydride in 5-cc portions, which are worked into the solution with a glass rod or thermometer. After all the acetic anhydride has been added, label the beaker, cover it with a watch glass, and place in an oven for 48 hours at 50° C. At the end of that time, divide the solution into two equal portions.

Part B. Preparation of Primary Acetates

Dilute one portion of the acetate solution with five 10-cc portions of glacial acetic acid. Gradually pour this diluted solution into 4 liters of water, with vigorous stirring. Wash the precipitated cellulose acetate by decantation with distilled water several times until free of acid. Squeeze the cellulose acetate dry by hand, and dry the acetate in an oven at 50° C. Bottle the sample, label, and use in Experiment 79.

Part C. Preparation of Secondary Acetates

To the other portion of the acetate solution add 15% of its volume of 50% acetic acid. Allow the mixture to stand at approximately 50° C for 12 to 16 hours. Pour the thick syrup into 4 liters of water and wash as in Part *B*. Dry the product in a 50° C oven. Bottle sample, and label for use in Experiment 79.

Part D. The Preparation of Cellulose Acetate-Butyrate

Treat 35 grams of cotton linters with a mixture of 35 grams of acetic acid and 35 grams of butyric acid for 4 hours at 40 to 43° C. Cool the mixture to 10° C, and add to it a mixture of 140 grams of butyric anhydride and 0.5 gram of sulfuric acid, previously cooled to 0° C. Allow the reaction to proceed for 4 hours, slowly increasing to a maximum temperature of 25° C during that time. Allow the mixture to react for 4 more hours at 25° C. A clear, extremely viscous dope should result. Add 35 grams of water to the mixture, and allow it to stand at 40 to 43° C for 24 hours. Precipitate the ester, wash, dry, etc.

QUESTIONS

1. What is the difference between a primary and a secondary acetate?
2. What is the function of the zinc chloride? Name other substances which serve the same function.
3. What is meant by the "degradation" of cellulose, and under what conditions is it most likely to occur?

4. How would you expect the properties of a cellulose acetate plastic to be related to the degree of degradation of the cellulose from which the acetate is prepared?
5. Discuss the molecular weight and acetyl content in cellulose acetate compositions used for fibers, sheeting, coating, plastics, etc.

Suggested Extensions

1. Consult the literature, and, using alkali cellulose, prepare the ethyl- or benzylcellulose ether. Compare these with the other cellulose derivatives.
2. Prepare and study the water-soluble cellulose derivatives, e.g., methylcellulose, ethylcellulose, hydroxyethylcellulose, and sodium carboxymethylcellulose.

EXPERIMENT 79

SOLUBILITIES OF CELLULOSE DERIVATIVES

Investigate the solubilities of commercial materials and products prepared in such a way as to fill in the following table.

Cellulose Derivatives—Laboratory Preparation

Solvent	*Primary Acetate*	*Secondary Acetate*	*Acetate Butyrate*	*Nitrate*
1. Water	....	....	....	....
2. Ethyl alcohol	....	....	....	....
3. Ether	....	....	....	....
4. Ether-alcohol (40 : 60)	....	....	....	....
5. Acetone	....	....	....	....
6. Amyl acetate	....	....	....	....
7. Chloroform	....	....	....	....
8. Benzene	....	....	....	....

Cellulose Derivatives—Commercial

	1	2	3	4	5
Solvent	*Primary Acetate*	*Secondary Acetate*	*Acetate Butyrate*	*Nitrate*	*Methyl*
1. Water	....	....	....	....	....
2. Ethyl alcohol	....	....	....	....	....
3. Ether	....	....	....	....	....
4. Ether-alcohol (40 : 60)	....	....	....	....	....
5. Acetone	....	....	....	....	....
6. Amyl acetate	....	....	....	....	....
7. Chloroform	....	....	....	....	....
8. Benzene	....	....	....	....	....

Solvent	6 Ethyl	7 Benzyl	8 Hydroxyethyl	9 Sodium Carboxymethyl
1. Water	....	....	....	....
2. Ethyl alcohol	....	....	....	....
3. Ether	....	....	....	....
4. Ether-alcohol (40 : 60)	....	....	....	....
5. Acetone	....	....	....	....
6. Amyl acetate	....	....	....	....
7. Chloroform	....	....	....	....
8. Benzene	....	....	....	....

QUESTION

1. Discuss the results obtained and their importance in the commercial applications, with particular reference to explosives, surface coating, fibers, continuous sheets, sizings, and molding compositions.

EXPERIMENT 80

PLASTICIZING OF CELLULOSE DERIVATIVES

Part A. Moldability of Unplasticized Cellulose Derivatives

Place the required amount of the following materials in a mold, and press the samples at 130° C and at 2000 to 3000 pounds per square inch. Cool the mold to at least 50° C before removing the specimen from the mold, and describe the condition of the molded sample.

	Condition of Molded Piece
1. Unplasticized cellulose acetate flake	....
2. Unplasticized cellulose acetate butyrate flake	....
3. Unplasticized ethylcellulose flake	....

Part B. Plasticized Cellulose Acetate

Cellulose acetate molding powders of different hardnesses, heat distortion, impact, flows, etc., are prepared by varying the amount and type of plasticizer used in the compositions. The following proportions are approximate for the composition indicated below.

Sample	*Hard* 1	*Medium* 2	*Soft* 3
Cellulose acetate	100	100	100
Dimethyl phthalate	18	23	28
Diethyl phthalate	18	23	28
Acetone	90	90	90

The commercial cellulose acetate should have an acetyl content of about 53%, and 125 to 175 seconds viscosity.

Procedure. Swell the cellulose acetate into a uniform gel by allowing the cellulose acetate and acetone to stand overnight in a covered beaker. Then mix thoroughly, either in a small mechanical mixer such as a Baker Perkins dough mixer or with a heavy stirrer, and blend in the plasticizers for 30 to 40 minutes. Process the mixture on differential rolls or a rubber mill, the front roll being heated with 10 to 15 pounds of steam and the rear roll cooled by running water. Process the mixture until the sample is free of acetone and free of bubbles. Remove the plasticized acetate sheet from rolls, and allow it to cool to room temperature. Grind the cooled sheet in a cutter-type mill. Bottle, and label the sample.

Part C. Plasticized Cellulose Acetate-Butyrate

Prepare the following two plasticized compositions in a manner similar to that above.

Sample 1.	Cellulose acetate-butyrate flake	80 parts
	Dibenzyl sebacate or methoxy ethyl stearate	40 parts
Sample 2.	Cellulose acetate-butyrate flake	60 parts
	Dibenzyl sebacate or methoxy ethyl stearate	40 parts

Process, grind, bottle, and label.

Part D. Plasticized Ethylcellulose

Prepare a sample of plasticized ethylcellulose, using the following proportions of materials:

Ethylcellulose	100
Japan wax	2
Fractol A	10
Phenyl-β-naphthylamine	1
Poly-pale ester gum	10

Blend the components in a beaker or suitable equipment thoroughly before milling directly without added solvents. The ethylcellulose should be of medium viscosity and between 46.9–48.5 ethoxyl content. The Japan wax may be substituted by any of the following.

Montan wax
Beeswax
Candelilla wax
Spermaceti wax
Carnauba wax
Opal wax
Tallow
Cetyl alcohol

The phenyl-β-naphthylamine may be replaced by other stabilizers, for example:

Dicyclohexylamine
Diphenylamine
Carbazole
Diphenylguanidine
p-phenylphenol
Vanillyl alcohol
Hydroquinone monobenzyl ether
Benzyl catechol

This composition may be plasticized without solvents directly on differential rolls or on a rubber mill, using 10 to 15 pounds of steam on the front roll and cold running water on the rear roll. Place the ethylcellulose blended with the compounding ingredients on the differential rolls, and process the mixture for approximately 15 minutes or until all the white specks in the mix have disappeared. Remove sheet, cool, grind, bottle, and label.

Part E. Moldability of Plasticized Cellulose Compounds

Mold samples *B*1, *B*2, *B*3, *C*1, *C*2, and *D* for 5 minutes at 2000 to 3000 pounds per square inch and at 130° C. Chill the mold to at least 50° C before removing molded samples. Compare these samples with the molded unplasticized samples.

QUESTION

1. Does cellulose acetate or cellulose acetate butyrate or ethylcellulose show plastic flow in the absence of a plasticizer?

Suggested Extensions

1. Study the plasticizer loss and the change in physical properties versus time at various temperatures.
2. Study the properties of a plasticized composition as the plasticizer ratio of dimethyl phthalate to diethyl phthalate is changed.

EXPERIMENT 81

GELS OF CELLULOSE DERIVATIVES

Part A. Ethylcellulose Gels for Casting

The following materials are used in the preparation of an ethylcellulose gel:

	Parts
Hercolyn	15
Coumarone resin	20
Microcrystalline wax	10
Iron oxide	20
Age Rite alba stabilizer	1

Heat all the ingredients together to 200° C in a 200-cc beaker and then rapidly add ethylcellulose, 35 parts. Stir rapidly to effect solution of the ethylcellulose. Then stop stirring to allow bubbles to rise, remove from the heat, and allow to cool to room temperature. Remove the plastic gel from the beaker as a solid mass, breaking the beaker if necessary. The mass can be remelted many times without decomposition and poured into non-porous molds for the preparation of cast forms and novelties.

Part B. Cellulose-Acetate Butyrate Gels for Coatings

Cellulose-acetate butyrate * molding powder	16–30 grams
Toluol	75 grams
Isopropyl alcohol	25 grams

* The cellulose-acetate butyrate used is Tenite II—201 formula.

The molding powder, toluol, and isopropyl alcohol are mixed in a 200-cc flask equipped with stirrer and reflux condenser and heated in a water or glycerol bath at 70° C until solution is completed. At this temperature the composition is a viscous fluid which on cooling to room temperature becomes a solidified gel. Coating is accomplished by dipping the article to be covered into the warm solution at 70° C and slowly withdrawing the article and allowing the volatile solvent to evaporate from the gel.

Immerse a glass rod or a pencil into the gel solution at 70° C, withdraw it slowly, and allow it to dry overnight.

EXPERIMENT 82

VULCANIZABLE PLASTICIZERS

Part A

To 80 parts of commercially plasticized cellulose acetate add 20 parts of diallyl phthalate containing 4 parts of benzoyl peroxide and blend to uniformity on milling rolls. Save a sample for control and cure the remainder in a mold at 125° C for one hour. Test the solubilities of the starting material and of the molded sample in the solvents listed below.

Part B

On milling rolls, prepare a uniform mixture of 80 parts of polyvinyl acetate and 20 parts of diallyl phthalate containing 4 parts of benzoyl peroxide. Save a sample and cure the remainder in a mold at 125° C for one hour.

Test the relative solubilities of the starting material and the molded sample in the following solvents:

	Solubility			
Solvent	*Original Sample A*	*Molded Sample A*	*Original Sample B*	*Molded Sample B*
Alcohol	....	....	....	....
Acetone	....	....	....	....
Ethyl acetate	....	....	....	....
Benzene	....	....	....	....

QUESTIONS

1. Explain the results obtained in the above tests. Is the whole mass insoluble or is the soluble component retained in an insoluble network?
2. What is meant by a vulcanizable plasticizer? Would not the term polymerizable plasticizer be more suitable?

EXPERIMENT 83

PREPARATION OF A SUPERPOLYESTER

Part A. The Preparation of the Superpolyester

In a three-necked flask, equipped with reflux condenser and a gas inlet tube, place 1 mole of adipic acid, 1.1 moles of ethylene glycol, and 0.5% of anhydrous zinc chloride, as calculated on the combined weight of acid and glycol. The reaction should be carried out under an atmosphere of hydrogen or deoxygenated nitrogen. If hydrogen is used, be careful of flames and explosion. A temperature of 200 to 210° C should be maintained by a suitable bath. Reflux the reaction for 2 hours under atmospheric pressure, and then change the reflux condenser to a position for downward distillation. Continue the heating for 10 hours, distilling off any material that comes over. At the end of 10 hours, reduce the pressure on the system by means of a good vacuum pump to 1 mm or less, and continue distillation with the bath at about 200° C until a sample of the reaction mixture has a zero acid number (Test Method 19). To arrive at this point, heating approximately 8 hours longer is necessary, and the reaction should be sampled every hour. A pure white waxlike solid should result.

Part B. Properties of the Superpolyester

Determine the solubility of this ester in alcohol, acetone, ethyl acetate, chloroform, and ether. Dissolve a sample of the polyester in chloroform, filter the solution, and concentrate to obtain crystals, using ether as a precipitant if necessary. Dry the sample free of solvent, and note its crystalline nature and its melting point.

Melting Point °C

Solubility in

Alcohol ....

Acetone ....

Chloroform ....

Ethyl acetate ....

Ether ....

QUESTIONS

1. Why is this resin called a superpolyester?
2. How does this superpolyester differ from the ethylene glycol succinate or phthalate prepared in Experiment 33?

Suggested Extensions

1. Determine what mol per cent of the glycol can be replaced by a trihydric alcohol such as glycerol before the characteristics of the superpolyesters are lost. Plot intrinsic viscosity versus mol per cent of the glycol.
2. Attempt to prepare a superpolyester using an ethylenic unsaturated dicarboxylic acid as maleic or fumaric acid.

EXPERIMENT 84

PREPARATION OF A SUPERPOLYAMIDE

The polyamide of this experiment may be prepared using either Preparations *A* or *B*. Preparation *A* is the preferred method since it gives results comparable to the industrial product, and the process is quite similar to the industrial method. However, it requires special pressure equipment which may not be available in many laboratories. If the equipment and time are available, it is suggested that both preparations be investigated and the resulting polymers compared.

Preparation A

This method involves: (1) a preformed salt of the diamine and the dicarboxylic acid, (2) a viscosity-controlling component, and (3) an autoclave constructed of special metals and (4) a deoxygenated inert gas.

1. Preparation of Hexamethylenediammonium Adipate. A mixture of 1 mole of hexamethylenediamine,* 1 mole of adipic acid, 1 liter of 95% ethyl alcohol, and 170 ml of water is warmed until complete solution occurs. The mixture is then cooled to separate the hexamethylenediammonium adipate in the form of white crystals, which are separated by filtration. Since the quality of the polyamide depends on the purity of the reactants, the salt is recrystallized from a mixture of 1 liter of ethyl alcohol and 170 ml of water. The melting point of the dried salt is 183 to 184° C.

2. Preparation of Hexamethylenediammonium Acetate. Dissolve 0.2 mole of hexamethylenediamine in 150 ml of 95% ethyl alcohol. With stirring, slowly add 0.4 mole of acetic acid. The acetate is separated by cooling and by the addition of petroleum ether or ethyl ether if required. The hexamethylenediammonium acetate is removed by filtration and recrystallized from 95% alcohol and small amounts of water.

The acetate salt is used in conjunction with the adipate salt to terminate the linear chains and thus control the viscosity of the polymer. If time does not permit the preparation of the acetate, it may be omitted since adipic acid may be used alone as a viscosity-controlling ingredient.

3. Preparation of the Polyamide. The autoclave used for the preparation may be either a silver-lined steel autoclave or one fabricated of 18 : 8 alloy steel (i.e., 18% chromium, 8% nickel, 74% iron). Nickel and monel metal are claimed to be unsatisfactory in the preparation of light-colored polyamides. While a stirrer is desirable for agitation during the reaction, it is not essential in the preparation of small amounts of polymer. Even with silver, chromium, or its alloys it is necessary to exclude oxygen during the reaction. The reactor is equipped with (1) an outlet leading to a condenser and receiver for collecting the water of reaction and (2) an inlet for introducing deoxygenated nitrogen

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* If hexamethylenediamine is not available, and time does not permit its synthesis, other diamines may be used to illustrate the principles involved in the preparation of superpolyamides. Though ethylenediamine does not produce good fibers when reacted with adipic acid, it may be used to illustrate the principle of the reaction, and the student may be left to use his judgment in deciding temperatures, time, etc.

into the reaction mass. The deoxygenated nitrogen is obtained by passing commercial cylinder nitrogen through this solution:

100	parts water
16.5	parts sodium hydrosulfite
13.3	parts sodium hydroxide
4.0	parts anthroquinone β-sodium sulfonate

The oxygen content of the nitrogen should be less than 0.03%.

The size of the reactor will determine the amount of ingredients to be used in the preparation of the polyamide. However, the ingredients are to be used in this ratio:

Hexamethylenediammonium adipate	100 grams
Hexamethylenediammonium acetate *	1 gram

* Adipic acid may be used instead of hexamethylenediammonium acetate as the viscosity stabilizer.

The purified ingredients are placed in a suitable high-pressure autoclave, after which the air is removed from the autoclave by evacuation and the autoclave is then filled with deoxygenated nitrogen. The autoclave is evacuated again and again filled with deoxygenated nitrogen to a pressure of 70 to 80 pounds. The autoclave is then heated to 285 to 290° C for 1.5 to 2 hours. The pressure is reduced slowly to atmospheric pressure during the course of 0.5 hour, and water distills from the reaction chamber. The heating is continued at 285 to 290° C for ½ to 1 hour under an atmosphere of deoxygenated nitrogen. A vacuum of 0.1 to 0.5 mm is applied and the heating continued for 1 to 1½ hours. The reaction mass is then cooled. Maintain the hot reaction product under an inert atmosphere while cooling. A solid white cake of polyamide, melting at about 248° C, should be obtained upon cooling. Its intrinsic viscosity will be about 0.8. The intrinsic viscosity is defined in the early chemical literature (see Exp. 41) as $\frac{\log_e \eta_r}{C}$, where η_r is the viscosity of a dilute (0.5%) solution of the polymer in *m*-cresol divided by the viscosity of the *m*-cresol in the same units and at the same temperature and C is the concentration in grams of the polymer per 100 cc of solution.

Preparation B

In a reaction flask, fitted with a gas inlet tube and a reflux condenser, place 1 mole of hexamethylenediamine and 1 mole of adipic acid. Place the material under an inert atmosphere of hydrogen or deoxygenated nitrogen, and keep it under this type of atmosphere throughout the reaction to prevent oxidation. Heat the reaction flask by means of a suitable bath to about 200° C to melt the reactants. Maintain the reaction mixture at a temperature of approximately 190 to 200° C or above the melting point of the reactants so that the mixture remains homogeneous. Allow the reaction to take place for 1½ to 2 hours.

At the end of this time change the condenser to a position for downward distillation, and dehydrate the reaction under a pressure of 40 to 50 mm at a temperature just above the melting point of the reaction mixture (approximately 280 to 285° C) for 6 hours, and for 6 hours more at 285 to 290° C at 1 or 2 mm vacuum. Cool the product. A white cake of superpolyamide is obtained.

1. Solubility Tests. Test the solubility of the superpolyamide (Test Method 17) in such common solvents as acetone, toluene, and alcohol. Investigate its solubility in hot phenol, hot formic acid, hot glacial acetic acid, and hot formamide, and observe if reprecipitation occurs on cooling. Note the melting point and the physical properties of the superpolyamide, and compare this sample to an industrial sample.

Properties

	Laboratory Sample	*Industrial Sample*
Melting Point	..........° C	....
Solubility in		
Acetone	....	....
Toluene	....	....
Alcohol	....	....
Hot phenol	....	....
Hot formic acid	....	....
Hot acetic acid	....	....
Hot formamide	....	....
Color	....	....

2. Tests on the Laboratory Preparation and Industrial Polymer.

a. Heat a glass rod to a sufficiently high temperature to melt but not char the superpolyamide. Touch the hot rod to the laboratory-prepared superpolyamide and draw out a fiber. Compare this to the industrial sample.

b. Place a small sample of about 0.5 gram of the superpolyamide in a test tube. Add 20 cc of concentrated hydrochloric acid and let it stand for at least 24 hours. Observe the condition of the sample at the end of that time and then heat on a water bath for one hour. Compare your sample to a sample of industrial polymer and to wool.

c. Repeat part *b* of the test, using 20 cc of 20% NaOH instead of concentrated hydrochloric acid.

d. Using tongs, burn a sample of the polymers over a Bunsen burner, note the odor, and compare this to the odor of wool or silk when burned.

e. Determine the melting point of a sample of wool or silk. Record the data in the following table, giving qualitative data as to the resistances, etc.

	Laboratory Superpolymer	*Industrial Sample*	*Silk or Wool*
Melting point	....	....	....
Resistance to HCl	....	....	....
Resistance to NaOH	....	....	....
Odor on burning	....	....	....

QUESTIONS

1. What is a superpolyamide? Why does it draw out into a fiber?
2. What is cold drawing? What property determines the fiber-forming ability of a polymer?

3. Refer to the chemical and patent literature on the superpolyamides, and determine what relation exists between intrinsic viscosity and fiber-forming qualities. What is a viscosity-controlling ingredient? Name some that may be used in the preparation of superpolyamides.
4. Are superpolyamides amorphous or crystalline?
5. Compare the structure of superpolyamides to the protein structure of natural fibers.
6. Give the equations for the acid and alkaline hydrolysis of the superpolyamide, including all intermediates.
7. From the literature show how the melting point of the superpolyamide is changed as the length of the carbon chain of the diamine or diacid is changed.
8. Show that the fiber-forming and cold-drawing properties are a function of molecular weight.
9. What results are obtained when metals are cold-drawn?

Suggested Extensions

1. Prepare a series of polyamides while keeping (*a*) the dibasic acid constant and varying the diamine and (*b*) keeping the diamine constant and varying the dibasic acid. Modify these reaction products with either monoamines or monoacids or amino alcohols.
2. Show that rubbery polyamides are obtained when the *N,N'*-dimethyldiamines are used in place of the unsubstituted diamino compounds.

EXPERIMENT 85

PREPARATION OF MIXED SUPERPOLY-ESTER-AMIDES

Part A. Preparation of the Superpolymers

Using the principles of Experiments 83 and 84, prepare mixed superpoly-ester-amides from the following ingredients.

	Mole Ratios			
Reactants	*I*	*II*	*III*	*IV*
Adipic acid	1	1	1	1
Hexamethylenediamine	0.5	0.3	0.7	0.9
Ethylene glycol	0.5	0.7	0.3	0.1

Part B. Proof of Intercondensation

Compare the following melted * mixtures of the superpolyester of Experiment 83 and the superpolyamide of the Experiment 84 with the three superpoly-ester-amides of Part *A*, using suitable solvents to prove that interpoly-ester-amides have been obtained in Experiment 85*A*.

	Mole Ratios		
	V	*VI*	*VII*
Superpolyamide of Exp. 84	0.5	0.3	0.7
Superpolyester of Exp. 83	0.5	0.7	0.3

QUESTION

1. Are the properties of the superpoly-ester-amides exhibited in proportion to their ester and amide content?

Suggested Extensions

1. Prepare a series of superpoly-ester-amides by reacting superpolyesters and a diamine.
2. Prepare a superpoly-ester-amide from a dibasic acid and an amino alcohol. Compare this polymer with the reaction product of a dibasic acid and a mixture of a diamino compound and a dialcohol having the same mole content of —NH_2 and —OH groups. As an example, compare 1 mole of aminoethanol with a mixture of ½ mole of ethylenediamine and ½ mole of ethylene glycol with the same dibasic acid.
3. Prepare a complete series of superpoly-ester-amides, changing the composition in very small steps. Show the point at which the crystallization forces are weakened and rubbery or elastic products are obtained.

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* Note that it is possible to prepare a superpoly-ester-amide by heating for a sufficient period of time a mixture of a superpolyester and a superpolyamide.

EXPERIMENT 86

PREPARATION OF PROTEIN RESINS

Part A. Hardened Proteins

Add 50 grams of soybean protein to 100 grams of formalin, the *p*H of which lies between 3 and 4, and allow the mixture to stand for 24 hours. Remove the excess formaldehyde solution by washing the protein with three 300-cc portions of water and air-dry the hardened protein for 24 hours; then dry at 60 to 70° C until the moisture content of the protein is about 10%. Mold the dry powder at 120° C at 2500 to 3000 pounds per square inch. Cool the mold before removing the molded piece. Determine the water absorption of the molded piece by immersion in cold water at room temperature for 24 hours.

Part B. Protein Fibers

1. **Spinning Solution.** Mix 12 grams of purified casein with 50 cc of water, and allow the mixture to stand for 15 to 30 minutes. Then add 1.8 grams of sulfonated vegetable oil or one of its soluble salts and 0.75 gram of sodium hexametaphosphate. Heat the mixture cautiously to effect solution. To the solution add, while stirring, 50 cc of an aqueous barium hydroxide solution containing 2.21 grams of barium hydroxide octahydrate. Filter the solution if pressure filtering equipment is available. This solution is labeled spinning solution. Let the spinning solution stand (ripen) overnight in a refrigerator.

2. **Precipitant and Hardening Solution.** Prepare the precipitation solution as follows. In 67 cc of water and in the following order dissolve 8 cc of concentrated H_2SO_4, 5 grams of formaldehyde, using the calculated amount of formalin, and 20 grams of dextrose.

3. **Fiber Preparation.** Using a hypodermic syringe and needle, and with the needle tip immersed in the solution, force some of the spinning solution into the precipitating solution so that the protein will be precipitated and filaments or fibers formed. Allow the fibers to remain in the precipitation solution approximately one hour. Decant the solutions from the fibers and wash several times with distilled water until neutral. Dry the fibers at 35° C. The fibers of this experiment will be somewhat brittle, and they demonstrate only the principles used in preparing protein fibers. The orifices used industrially are of the order of two thousandths to seven thousandths (0.002 to 0.007) of an inch in diameter. The commercial preparation of fibers likewise includes a stretching operation which increases the strength of these fibers made from polymers which can be oriented by drawing.

Part C. Protein Films

Pour some of the spinning solution used for the preparation of fibers onto a small glass plate and allow it to dry at room temperature for 10 to 24 hours before submersion in the precipitant and hardening solution for one hour. Decant the hardening solution from the film and wash several times with distilled water until neutral. Dry the film at room temperature.

QUESTIONS

1. What is the function of (*a*) the sulfuric acid, (*b*) the formaldehyde, (*c*) the dextrose in the precipitating solution?
2. What is acid casein? What is rennet casein?
3. Discuss other proteins that have been converted into fibers.
4. Discuss the viscose spinning process.
5. Why does stretching increase the strength of some fibers?

Suggested Extension

1. Blend the hardened proteins with phenol alcohols before molding, and note the change in the properties of the resin.

EXPERIMENT 87

PREPARATION OF MONO- AND POLYSULFONAMIDE RESINS

Benzenesulfonamide versus Benzenedisulfonamide

Resin A. Prepare a resin by refluxing 23.6 grams of benzenedisulfonamide with 17 grams of formalin adjusted to a *p*H of about 6. At the end of a 15-minute reflux period, resin precipitation should occur. Allow the mixture to cool, decant the water layer, and wash the residue with about 100 cc of distilled water by rewarming the resin and water in the flask. Recool, decant the water thoroughly, and dissolve the resin in 95% ethyl alcohol to obtain a 50% resin solution.

Resin B. Repeat *A*, but reflux for at least 30 minutes and treat as *A*. If the resin is not soluble in alcohol, test its solubility in ketones, e.g., acetone.

Resin C. Repeat *A*, using benzene- or toluenesulfonamide with at least 1 mole of formaldehyde per mole of sulfonamide, and prepare a resin varnish in a suitable solvent. Test such solvents as alcohol, acetone, and dioxane.

Tests

Treat all the varnishes for cure on a hot plate at 140 to 150° C and observe the changes, if any, in the resins. Repeat the cure tests, using a small amount of phthalic anhydride and sodium chloroacetate as a curing accelerator. On glass plates prepare films of these varnishes with and without curing accelerators and bake at 100 to 110° C for at least 24 hours.

Test resistance of the baked films to hot and cold acetone, alcohol, and water. Record the results obtained in the table below.

		Solubility of Cured Film		
	Hot Plate	*Acetone*	*Alcohol*	*Water*
	Cure at 150° C	*Hot Cold*	*Hot Cold*	*Hot Cold*
Resin *A*	....	....	....	....
Resin *A* + phthalic anhydride	....	....	....	....
Resin *A* + sodium chloroacetate	....	....	....	....
Resin *B*	....	....	....	....
Resin *B* + phthalic anhydride	....	....	....	....
Resin *B* + sodium chloroacetate	....	....	....	....
Resin *C*	....	....	....	....
Resin *C* + phthalic anhydride	....	....	....	....
Resin *C* + sodium chloroacetate	....	....	....	....

QUESTIONS

1. Give the synthesis of benzenesulfonamide and benzenedisulfonamide.
2. Write the structure of a benzenesulfonamide-formaldehyde resin. Is it a thermoplastic or thermosetting resin? Contrast this with the reaction product of a polysulfonamide-aldehyde resin, and discuss the differences in terms of functionality.
3. Does an acid catalyst accelerate the cure of the sulfonamide resins? If it does, should the initial condensation be carried out under acid or alkaline conditions?

Suggested Extension

1. Modify the urea and melamine resins with the sulfonamide compounds.

EXPERIMENT 88

FUNCTIONALITY OF ARYL AMINO COMPOUNDS

Part A

By means of a separatory funnel, add slowly, with stirring, 1 mole of aniline to 1 mole of formaldehyde, using the calculated amount of formalin. Let the mixture stand, and continue stirring until the reaction produces a solid material. Filter the precipitate, wash with water, and dry in an oven at 75° C.

Part B

Dissolve 1 mole of aniline in the calculated molar equivalent of concentrated hydrochloric acid. Cool the acid solution to room temperature, and add slowly 1 mole of aqueous formaldehyde, using the calculated amount of formalin. Let the mixture stand for 1 hour, then neutralize it slowly with 1 mole of sodium hydroxide in a 20% aqueous solution. Remove the precipitate by filtration and disperse in fresh water. Repeat the washings until the precipitate is free of chloride ions. Filter the precipitate, and dry as in Part *A*.

Part C

Reflux 1 mole of sulfanilamide with 2 moles of formaldehyde, using formalin solution, for 30 minutes. Cool, decant the aqueous layer, and wash with warm water. Isolate the condensation product and dry as in Part *A*.

Part D

Add 1 mole of sulfanilamide to 1 molar equivalent of concentrated hydrochloric acid, cool the solution to room temperature, and add slowly 2 moles of aqueous formaldehyde, using formalin solution. Let the mixture stand for 1 hour, then neutralize slowly with 1 mole of 20% aqueous sodium hydroxide. Remove the precipitate by filtration and disperse in fresh water. Repeat the washings until the precipitate is free of chloride ions. Filter the precipitate and dry as in Part *A*.

Part E

Reflux 1 mole of an aminophenol, e.g., *p*-aminophenol, with 2 moles of formaldehyde for 15 minutes. Isolate the resin, dry, etc., as in Part *A*.

Part F

Dissolve 1 mole of aminophenol in 1 mole of concentrated hydrochloric acid and react at room temperature with 2 moles of formaldehyde as in Part *D*. Isolate and dry the condensation product.

Test the above resins for solubility in ethyl alcohol, acetone, butyl acetate, and toluene. Heat the resins to 150° C on the hot plate for at least 5 minutes and note whether (*a*) a melt is obtained, (*b*) the material cures, and (*c*) the cured material is soluble. Record the results in the following table:

Resin	*Description of Resin*	*Solubility*			*Resin at 150° C*		*Solubility of Cured Resin*
		Acetone	*Alcohol*	*Benzene*	*Melt*	*Cure*	
A	....	....	....	....	......	......	....
B	....	....	....	....	......	......	....
C	....	....	....	....	......	......	....
D	....	....	....	....	......	......	....
E	....	....	....	....	......	......	....
F	....	....	....	....	......	......	....

QUESTIONS

1. Give the syntheses of aniline, the *o*-, *m*-, and *p*-aminophenols and sulfanilamide.
2. What is anhydroformaldehyde aniline? Write the structure of an aniline-formaldehyde resin. Does it produce a thermoplastic or thermosetting resin when polymerized?
3. How does attaching another aldehyde reactive group to the benzene nucleus of aniline affect its reactivity with formaldehyde, and how does it change the nature of the resin?
4. Describe the differences in the resinification of the amino compounds of this experiment in the absence and presence of added acid catalysts.
5. What type of resin should be obtained from a diaminobenzene and formaldehyde?

Suggested Extensions

1. Study the differences in the acid and alkaline catalysis of aniline, aminophenol, and sulfanilamide.
2. Study the effect on the above three amino compounds by first causing the aldehyde reaction with their hydrochlorides, then neutralizing the condensation with alkali.
3. Study the differences between the resins obtained by condensing *o*-, *m*-, and *p*-aminophenols with formaldehyde and other aldehydes.

EXPERIMENT 89

POLYMERIZED FURFURYL ALCOHOL

Part A. Effect of Catalysts

Place 10 cc of freshly distilled furfuryl alcohol in each of eight 50-cc test tubes supported in a rack. Number the tubes 1 to 9 consecutively. Add the following quantities of reagents to each tube. Observe the tubes every 15 minutes for 2 hours, and then at the end of about 24 hours.

Caution. Keep test tubes pointed away from your eyes as some of these reactions may become violent.

		Condition of Sample	
Tube	*Reagent*	*2 Hours*	*24 Hours*
1	None	....	....
2	0.1 gram of oxalic acid	....	....
3	0.1 gram of choloracetic acid	....	....
4	0.1 cc of concentrated phosphoric acid	....	....
5	0.05 cc of concentrated HCl	....	....
6	0.1 cc of concentrated HCl	....	....
7	0.2 cc of concentrated HCl	....	....
8	0.1 cc of 35% H_2SO_4	....	....
9	0.1 gram of toluene sulfonic acid	....	....

Part B. Furfuryl Alcohol Coatings

Pour a small quantity of concentrated hydrochloric acid in a beaker. By means of a tongs immerse a piece of cotton waste into the acid, and with the saturated cotton waste paint one flat side of a piece of wood of approximate dimensions 3 by 3 by 1 inch with concentrated hydrochloric acid. Let the acid-coated wood stand about 5 minutes and then paint the same surface with furfuryl alcohol. When the coating feels dry, repeat the acid treatment and the furfuryl alcohol coating until a solid black uniform coating on the wood is obtained. After the final coating, allow the wood to stand for about 3 days at room temperature and then test the surface resistance with concentrated and dilute acids and alkali and the solvents listed below. The test is performed by placing a drop of the

reagent on the surface of the coated wood and observing any change that takes place on the surface within 24 hours. Record the test data in the following table:

Reagent	*Surface Resistance*
Concentrated sulfuric acid	....
Dilute sulfuric acid	....
Concentrated sodium hydroxide	....
Dilute sodium hydroxide	....
Concentrated acetic acid	....
Benzene	....
Acetone	....
Alcohol	....

QUESTIONS

1. Is the formation of the resin due to a condensation or addition polymerization reaction? Or both?
2. Write the probable structure of the furfuryl alcohol polymer.
3. Compare this to the structure of the indene and coumarone resins.
4. How does the nature and quantity of acid influence the polymerization of furfuryl alcohol?

Suggested Extensions

1. Study the comparative polymerizations of furane, furfuraldehyde, furoic acid, and ethyl furoate alone and as modifying agents in the polymerization of furfuryl alcohol.
2. Prepare furfuryl alcohol polymers in the presence of such soluble resins as polyvinyl butyral.

EXPERIMENT 90

PREPARATION OF A COUMARONE-INDENE RESIN

Part A. Resin from Undiluted Coumarone-Indene

Cool 50 cc of well-stirred commercial coumarone-indene fraction of coal tar to 0° C and add slowly, dropwise, 3 grams of sulfuric acid of 1.84 specific gravity. Ten minutes after all the acid has been added, dilute the solution with 500 cc of cold water. Allow the mixture to settle for about 15 minutes. Decant off the top oil, leaving behind any heavy tar. Neutralize the decanted oil with a 20% sodium hydroxide solution. Separate the NaOH solution from the oily layer in a separatory funnel. Wash the oily layer three times with an equal volume of 3% HCl and once with distilled water. Distill the resulting oily material in vacuo until the melting point of the residual resin has risen to 125 to 135° C. Pour the resin into cooling pans. Break up the cooled resin, bottle, and label.

Part B. Resin from Diluted Coumarone-Indene

Repeat directions for resin *A*, having first diluted the indene with an equal portion of solvent naphtha.

Part C. Comparison of Resins

Test the solubility of the two resins prepared in a series of the following selected solvents and record the melting points of the resins.

Solvent	*Melting Point*	*Resin A Solubility* ____° C	*Resin B Solubility* ____° C
1. Acetone	....	....	....
2. Alcohol	....	....	....
3. Benzene	....	....	....
4. Mineral oil	....	....	....
5. Linseed oil	....	....	....
6. Tung oil	....	....	....

QUESTIONS

1. What are the formulas of coumarone and indene, and from what sources are they derived?
2. Indicate the possible structures of: a coumarone resin, an indene resin, and a coumarone-indene resin.
3. How does dilution of the coumarone-indene produce a better polymer?

Suggested Extensions

1. Study the molecular weight of the polymer as a function of (*a*) catalyst concentration, (*b*) stannic chloride as a catalyst, (*c*) boron trifluoride as a catalyst.
2. Study the addition of inert hydrocarbon diluents of the aliphatic and aromatic series to the polymerization of the coumarone-indene mixture.
3. Prepare styrene-modified coumarone-indene resins.
4. Prepare a pure coumarone polymer and a pure indene polymer and compare mixtures of these to a coumarone-indene interpolymer.

EXPERIMENT 91

HARDENED ROSIN AND SHELLAC

Part A. The Liming of Rosin

Heat 20 grams of technical rosin in a 100-cc beaker to 300° C until the rosin melts. Stir the liquefied rosin mechanically, and after the 300° C temperature has been reached, the rosin is allowed to cool to 200° C. While maintaining this temperature, and with stirring, gradually add 1.2 grams of hydrated lime. The temperature is then raised to 250° C. When all the water has been driven off, the limed rosin is poured into cooling pans. Cool, break up the limed rosin, bottle, and label.

Compare the melting point, the acid number, and the solubility of the limed rosin with a sample of the original untreated rosin (Test Method 26) and record the data in the following table.

	Rosin	*Limed Rosin*
Melting point	....	....
Acid number	....	....
Solubility in solvent naphtha	....	....
Solubility in alcohol	....	....
Solubility in acetone	....	....
Immersion in water	....	....

Dissolve 1 gram of limed rosin in a small amount of petroleum naphtha. Spread a film of this material on a wooden test block or glass plate and allow it to dry at room temperature for at least an hour. Then continue drying at 75 to 100° C in an oven for at least an hour. When dry, immerse it in water for an hour at room temperature. Compare the effect of water on the limed-rosin sample with a similar film of untreated rosin.

Part B. The Hardening of Shellac

Determine the acid number of a sample of shellac, and calculate how much lime can combine with shellac. Lime the shellac according to the general principles of Part *A*, modifying the conditions, if necessary, after a few preliminary experiments. Repeat the experiment, using zinc oxide as a hardening agent. Test the melting point and solubility of shellac, limed shellac, and zinced shellac in methyl and ethyl alcohol.

QUESTIONS

1. What is shellac? Qualitatively, how does it compare with rosin in reactivity?
2. What are the chemical formulas for the major components of shellac?
3. Where and how is rosin obtained?
4. What is rosin chemically?
5. What occurs on liming of rosin?
6. Write the formula for abietic acid.
7. What is gloss oil, and what are its uses?
8. What is petroleum naphtha?

EXPERIMENT 92

ROSIN DERIVATIVES AND COMPLEXES

Part A. Preparation of Ester Gum

In a round-bottomed flask, fitted with a separatory funnel, mechanical stirrer, and reflux air-cooled condenser, place 100 grams of rosin and 0.02 gram of powdered zinc chloride. Heat to 200° C, and begin adding slowly, drop by drop, 12 grams of glycerol. When all the glycerol has been added, raise the temperature to 310° C to remove excess glycerol. When no more glycerol distills off through the reflux condenser, pour the reaction mixture into a cooling pan. Break up the ester gum, bottle, and label.

Compare the melting point, acid number, and the alcohol and naphtha solubilities of the ester gum with unesterified rosin.

	Rosin	*Ester Gum*
Melting point	....	....
Acid number	....	....
Alcohol solubility	....	....
Naphtha solubility	....	....

After suitable solvents have been determined, compare films prepared from rosin, limed rosin, and ester gum by pouring solutions on glass plates, air-drying for an hour, and then drying at 70 to 80° C for an hour in an oven. Test the film by immersion in water at room temperature for 24 hours and in boiling water for 15 minutes.

	Appearance and Hardness		
Sample	*Initial*	*Immersion in Cold Water*	*Immersion in Boiling Water*
Rosin	....	....	....
Ester gum	....	....	....
Limed rosin	....	....	....

Part B. Ester Gum-Phenol Resin Complexes

In a suitable container heat 5 grams of ester gum to 200 to 250° C, until a clear melt is obtained, and then cool to 175 to 178° C. In small portions, slowly add, with stirring, 5 to 10 grams of any of the following dialcohols: (*a*) butylphenol dialcohols, (*b*) amylphenol dialcohols, or (*c*) the styrylphenol dialcohols (Experiment 19). Add the portions of the phenols slowly and not before most of the foaming resulting from the previous addition ceases. Pour the reaction mixture into a cooling pan, break up the resin, bottle, and label the sample, and record the test data in the following table.

	Ester Gum	*Phenol Complex*
Melting Point	____° C	____° C
Solvent	*Solubility*	
Alcohol	....	....
Acetone	....	....
Benzene	....	....
Solvent naphtha	....	....
Tung oil	....	....
Linseed oil	....	....

Part C. Varnish Preparation

Refer to Experiment 21 and, by the same procedure, prepare two varnishes using ester gum in contrast to the ester gum-phenol alcohol complex in the following proportions:

Varnish A		*Varnish B*	
Linseed oil	40 grams	Linseed oil	40 grams
Ester gum	20 grams	Ester gum-phenol alcohol complex	20 grams

Body these resins to an 8-inch string, dilute with solvent, and then add 0.75 gram of driers as in Experiment 21. Prepare air-dried films and compare the quality of the two films.

	Varnish A	*Varnish B*
Tack-free (time)	....	....
Hard and dry (time)	....	....
Type of film	....	....
24-hour immersion, cold water	....	....
15-minute immersion, boiling water	....	....

QUESTIONS

1. Write the reaction between abietic acid and ethylene glycol; between abietic acid and glycerol. What are the commercial products thus prepared, and what are their uses?
2. Does the addition of the phenol dialcohols raise the softening point of the ester gum? Does the ester gum-phenol alcohol complex cause the bodying of drying oils at a faster rate than ester gum alone?

Suggested Extension

1. Study the change in melting point of ester gum as the proportions of phenol-dialcohols are changed.

EXPERIMENT 93

RESIN-IMPREGNATED AND COMPRESSED WOODS AND PLYWOODS

Part I. Phenolic Resins

A. Impregnation of Veneers. Prepare a large sample of water-soluble varnish according to Experiment 9. In this varnish immerse, edgewise, 33 sheets of 0.025-inch birch veneer cut to 6 by 6 inches. The veneer can be kept immersed by suitable weights. At the end of 8 hours' immersion, remove the veneers, and let them drip for 10 to 15 minutes. Cover the treated veneer with glassine paper or moistureproof cellophane for a 24-hour diffusion period in a cool place. Next dry the impregnated veneers in an air-circulating oven at 60 to 65° C for 10 hours. Determine the percentage of resin in the impregnated wood by weighing an untreated piece which has also been dried for 10 hours at 60 to 65° C.

B. Preparation of Resin-Impregnated Plywood. Lay the veneers in a plywood construction with the grains of the adjacent veneers at right angles to each other. Place the load between press pans which have been dusted with zinc stearate, and press at 1000 pounds per square inch at 150° C for 20 minutes. The load is slowly cooled to room temperature while under pressure, and then removed. The thickness of the final panel is approximately one-fourth inch.

Part II. Urea Resins

A. Preparation of Urea Syrup. Prepare a solution of sesquimethylolurea as follows, using the stated proportions.

Add 100 grams of dimethylolurea and 30 grams of urea to 400 cc of water and, with stirring, slowly heat the mixture to 75 to 80° C, until a clear solution is obtained. Allow the mixture to cool to room temperature. The solution does not need to be filtered if only a slight turbidity exists in the solution.

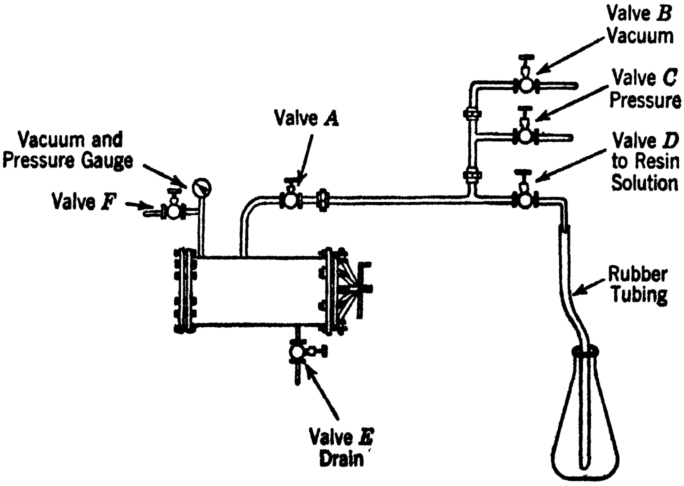


FIGURE 9. Wood Impregnation Apparatus.

B. Vacuum and Pressure Impregnation of Wood. Prepare five blocks of soft pine of about the dimensions ½ by 3 by 6 inches, and place them in a pressure and vacuum treating equipment, as shown in Figure 9.

To assure immersion in the solution later on in the process, cover the wood with a metal screen and weight down with metal. Lock the pressure bolts, open valves *A* and *B*, close all other valves, and vacuum-treat the wood at 25 to 30 inches of Hg for at least 60 minutes. Then shut off valves *A* and *B*. Immerse the rubber tubing from valve *D* to the bottom of the reservoir of urea syrup and open valve *D*. Then, *slowly* open valve *A*, making sure that the rubber tube is immersed to the bottom of the reservoir so that no air enters the equipment until all the solution is in the treating vessel. Shut off valve *D* and slowly open valve *C* to permit air pressure to enter the treating chamber. Pressure-treat the wood at 50 to 75 pounds per square inch for at least an hour. Shut off the valve *C* and open valve *F* to permit air pressure to be reduced to atmospheric pressure. Open valve *E* to drain off the solution. Open the pressure tanks, remove the wood, and let drip for 10 or 15 minutes. Cover the treated wood with glassine paper or moisture-proof cellophane or a rubber blanket for a 24-hour diffusion period in a cool place. Next dry the impregnated woods in an air-circulating oven at 50 to 55° C for 24 hours. Label these samples II *B*.

C. Curing of Impregnated Woods. Treat the impregnated woods as follows.

Sample II B–a. Oven-cure two pieces of impregnated samples II *B* to the following schedule.

Temperature	*Time, Hours*
60° C	10
70° C	10
90° C	10
110° C	5
130° C	3
140° C	1

Sample II B–b. Prepare a compressed and cured sample by placing one piece of impregnated wood (Sample II *B*) between press pans in a cold press. Turn on the heat and cure at 140° C for 20 minutes at 800 to 1000 pounds per square inch. The panel is slowly cooled to room temperature while under pressure, and then removed.

Sample II B–c. Preheat one piece of impregnated wood (Sample II *B*) at 60° C for 24 hours. Then compress and cure as in Sample II *B–b*.

Tests. Determine water absorption for 24 hours, water resistance for 1 hour in boiling water, and chemical resistance by immersion for 24 hours in 10% NaOH and 10% HCl for all the wood samples prepared. Record also their relative hardness, using 10 as the hardest and 1 as the softest. Record the data in the following table:

Sample	*24-Hour Water Absorption*	*15 Minutes Boiling Water*	*Dilute HCl*	*Dilute NaOH*	*Hardness*
Untreated veneer	....	....	....	....	....
Sample I *B*	....	....	....	....	....
Untreated pine	....	....	....	....	....
Sample II *B*	....	....	....	....	....
Sample II *B–a*	....	....	....	....	....
Sample II *B–b*	....	....	....	....	....
Sample II *B–c*	....	....	....	....	....

QUESTIONS

1. Outline suitable control methods for an exacting manufacture of impregnated and compressed woods and plywoods.
2. Discuss the necessity for the long impregnation period and for the conditioning or diffusion period as compared to the impregnation of paper or fabric. In this discussion consider the structure of the wood, etc.

EXPERIMENT 94

PREPARATION OF A PHENOLIC RESIN ADHESIVE

Reflux for 1 hour 94 grams (1 mole) of phenol, 100 grams of formalin (approximately 1.25 moles of formaldehyde), and 1 gram of barium hydroxide octahydrate. Cool the resin to room temperature, neutralize the solution by bubbling CO_2 gas through it until no more gas is absorbed. Filter off the barium carbonate and dehydrate under a 20-inch vacuum to 80 to 83% resin content. Cool the resin, and pour it into a suitable container.

To 10-gram samples add by means of a small burette the following percentages of concentrated hydrochloric acid solution (30% HCl) and stir with a thermometer for 3 minutes. Then set to one side for observation. Note any temperature rise during stirring.

Sample	*Percentage*	*Temperature Rise*	*Time to Set*
1	0.5	....	....
2	1	....	....
3	2	....	....
4	3	....	....
5	5	....	....
6	7	....	....
7	9	....	....

Select the sample which has approximately a 3- to 4-hour stability working life and prepare a new sample of this composition.

Prepare two panels by spreading 2 grams of this adhesive resinous composition on one side of each 6 by 6 inch piece of 0.050-inch birch veneer. Clamp the two pieces together with the resin-coated sides facing and in contact with each other, but with the wood grain at right angles to each other. Let the panels remain clamped for at least 24 hours. At the end of that time, cut a sample from the laminated wood and boil it in water to failure. Cut another sample and bake for an hour at 60° C before boiling to failure. Note the time of failure, and compare this to an animal glue or casein glue bonded wood sample.

QUESTIONS

1. What do the results obtained tell about the reactivity of methylolphenols in acid and alkaline conditions?
2. Why was the bulk of the water removed before using the resin as an adhesive?
3. How would this resin be used as a low-pressure laminated resin?

Suggested Extension

1. Study the addition of resorcinol, 1,3,5-xylenol, phenolsulfonic acid, etc., alone or in the presence of paraformaldehyde to the dehydrated resin, and determine if acceleration of curing is accomplished.

EXPERIMENT 95

PREPARATION OF AN AMINOPLAST RESIN ADHESIVE

Reflux 161 grams of formalin (2 moles of formaldehyde), 6 grams of 28% ammonia (0.1 mole of ammonia), 0.04 gram (0.001 mole) of sodium hydroxide which is dissolved in water to give a 10% solution, and 60 grams (1 mole) of urea for 2 hours. Mix the ingredients in the order stated. Dehydrate under a 20-inch vacuum to a 75 to 78% solids content, and pour the resin into a suitable container.

Determine the most suitable accelerator and the amount of 30% solution to be used to give a 3- to 4-hour life from the following list of reagents:

30% Solution	*Reagents, cc*	*Life in Hours*
Ammonium chloride	....	....
Acetic acid	....	....
Hydrochloric acid	....	....
Phosphoric acid	....	....
Ammonium sulfamate	....	....
Glycine	....	....

Parallel the details of Experiment 92 for the cementing of wood panels. Compare the results with the results obtained in Experiment 92.

QUESTION

1. Are the urea resin adhesives as water resistant as the phenolic resins?

Suggested Extensions

1. Study resorcinol and 1,3,5-xylenol as an accelerator for the urea resin adhesives.
2. Study melamine resins or melamine-modified urea resins as adhesives.

EXPERIMENT 96

PREPARATION OF AN ANION EXCHANGE RESIN

Dissolve 1 mole of metaphenylenediamine in 1.1 moles of hydrochloric acid dissolved in 1 liter of water. Add 1.5 moles of formaldehyde, using the calculated amount of formalin. Let the solution stand at room temperature until a gel is formed. Dry the gel at 80 to 90° C. Treat the dried gel with a 10% ammonia solution, and wash it free of salts and excess ammonia with distilled water. Dry the washed gel at 80 to 90° C in an oven.

Prepare a 0.03 molar solution of hydrochloric acid, and measure its *p*H. To 100 cc of this solution add the following indicated amounts of resin, and redetermine the *p*H of the solution after the resin has been in contact for 10 minutes and after removing the resin by filtration. Also test the filtrate for chloride ions.

Sample	*Amount Resin, Grams*	*pH*
1	0.01	....
2	0.10	....
3	0.3	....
4	0.5	....
5	1.0	....
6	2.0	....
7	10.0	....

QUESTIONS

1. Using ionic equations, show how the anion exchange resins function.
2. How is the resin regenerated?
3. How could this resin be used to purify water containing undesirable anions?
4. What are zeolites?
5. List the requisite properties of an ion exchange resin.

Suggested Extensions

1. Prepare ion exchange resins by reacting phenol alcohols with aliphatic and aromatic polyamines.
2. Study the use of melamine in ion exchange resins.

EXPERIMENT 97

PREPARATION OF A CATION EXCHANGE RESIN

Dissolve 100 cc of formalin in 30 cc of concentrated hydrochloric acid, and add this solution to a boiling solution of 50 grams of quebracho tannin in 500 cc of ethyl alcohol.

Continue the reflux until the resin is completely precipitated. Cool the mixture, filter, wash with distilled water, and dry at 100° C.

Prepare a solution of sodium hydroxide containing 1 part of sodium hydroxide per 10,000 parts of water. Measure the *p*H of the solution. To 100 cc of this solution add the following indicated amounts of resin. Let the mixture stand for 10 minutes, filter, redetermine the *p*H of the solution, and titrate the filtrate for sodium hydroxide content.

Solution	*Resin, Grams*	*pH After Treatment*
1	0.01	....
2	0.1	....
3	0.5	....
4	1.0	....
5	2.0	....
6	10.0	....

QUESTIONS

1. Using ionic terms, show how cation resins function. How would the resin be regenerated?
2. How would you use a combination of anion and cation exchange resins to obtain pure water?

Suggested Extensions

1. Prepare ion exchange resins by reacting the phenolsulfonic acids with phenol alcohols or with phenol and formaldehyde.
2. Sulfonate a heat-converted phenol-formaldehyde resin.
3. Sulfonate an insoluble divinylbenzene polymer or copolymer.

TEST METHODS

Whenever possible, methods should be A.S.T.M. ones. Some of the following test methods have been revised in an effort to save time. These revisions likewise make an attempt to realize that many laboratories may not be equipped with or cannot afford to purchase standard equipment. In these cases the revised methods sacrifice a standardization but not the principles of the tests.

TEST METHOD 1

FORMALDEHYDE DETERMINATION, USING HYDROXYLAMINE HYDROCHLORIDE

This method depends on the determination of the hydrochloric acid formed when formaldehyde reacts with hydroxylamine hydrochloride according to the following reaction:

$$CH_2O + NH_2OH \cdot HCl \rightarrow H_2O + CH_2 = NOH + HCl$$

For determinations in non-aqueous systems, as in precipitated resin layers, non-reactive solvents, such as ethyl alcohol and dioxane, are used to insure the solubility of the resin. For accurate determinations it is important that blank determination be made on the reagents and a correction included for this value.

Before the addition of the hydroxylamine hydrochloride, it is essential that the solution of aldehyde be made neutral to the indicator used in the final titration. This neutralization is accomplished by the addition of either acid or alkali, depending on the *p*H of the solution to be tested. Hydrochloric acid and sodium hydroxide solutions of about 0.3 to 0.5 *N* are satisfactory. The indicator used is a 1% alcoholic solution of bromophenol blue. The aldehyde sample is best delivered from a graduated 1-cc pipette, with a relatively large opening for viscous resins solutions.

Procedure

Add 1 cc of the sample to be tested for aldehyde to 20 cc of alcohol in a 100- to 125-cc Erlenmeyer flask containing 3 drops of 1% alcoholic bromophenol blue. Neutralize with acid or alkali as required, checking the end point by over-titration and back-titration if necessary. Add 7 cc of 10% aqueous hydroxylamine hydrochloride, shake, and let stand for 5 to 10 minutes. Titrate to neutrality with ⅓ *N* NaOH. Record the cubic centimeters of NaOH used. Run a blank on the reagents used, and record the cubic centimeters of alkali used. The final color of the indicator should be duplicated both in the blank and in the sample. Likewise, this method is not too accurate for low formaldehyde concentrations, and, therefore, correspondingly larger samples should be taken so that the "cc of titrant" can be determined on the burette with the same degree of accuracy in each case.

Resin sample .... cc ⅓ *N* NaOH

Blank sample .... cc ⅓ *N* NaOH

Cubic centimeters of titrant = Resin − Blank ....

Calculations

A. When NaOH is exactly $\frac{1}{3}N$ and exactly 1 cc of sample was used:

Cubic centimeters of titrant = Grams of CH_2O per 100 cc of solution

B. When sample is not 1 cc or the NaOH is not $\frac{1}{3}N$, the calculations become:

$$\frac{3.0 \times \text{Cubic centimeters of titrant} \times \text{Normality NaOH}}{\text{Cubic centimeters of sample used}} = \text{Grams of } CH_2O \text{ per 100 cc of solution}$$

TEST METHOD 2

FORMALDEHYDE DETERMINATION, USING SODIUM SULFITE

This method depends on the determination of the sodium hydroxide formed when formaldehyde reacts with the sodium sulfite as follows:

$$H_2O + CH_2O + Na_2SO_3 \rightarrow HOCH_2SO_3Na + NaOH$$

Since the sodium sulfite solution is unstable, *it must be renewed every 48 hours.* For this reason Test Method 1 is more widely used whenever applicable.

Prepare the following reagents:

A. Dissolve 1 gram of corallin * in 400 cc of a 50% aqueous methyl alcohol solution.

B. Dissolve approximately 63 grams of sodium sulfite heptahydrate crystals in sufficient distilled water to make 250 cc or approximately 2 *N* solution.

C. Dissolve Reagent Grade sulfuric acid in water to prepare a *N* solution.

Procedure

Add 10 cc of the formaldehyde containing solution at 20° C from a burette or pipette to about 100 cc of distilled water in a 500-cc volumetric flask, adding ethyl alcohol, if necessary, to maintain solution. Add a few drops of corallin solution and neutralize as in Test Method 1 with acid or alkali as required, checking the end point by over-titration and back-titration if necessary. Make the flask up to mark with distilled water. Measure out exactly 100 cc of this solution, and add to it 50 cc of the sodium sulfite solution and about 2 drops of corallin indicator. Mix thoroughly, and let stand for about 10 minutes before titrating to the disappearance of color with the *N* sulfuric acid solution. Record the cubic centimeters of acid used. When great accuracy is not required, the 10-cc sample may be at room temperature instead of at 20° C. Run a blank replacing the 100 cc of formaldehyde solution with either distilled water or a mixture of distilled water and alcohol in the proportions used in the experiment. Record the cubic centimeters of acid used in blank.

Cubic centimeters of H_2SO_4 used on sample ....

Cubic centimeters of H_2SO_4 used on blank ....

Cubic centimeters of H_2SO_4 for calculations ....

---

* Corallin is also known as aurine or rosalic acid.

Calculation

1.5 × Cubic centimeters of H_2SO_4 × Normality H_2SO_4

= Grams of CH_2O per 100 cc of solution

Modified Procedure

Smaller samples of solutions may be used. Record the weight of 1 cc of a sample of the formaldehyde solution added to a tared flask. Add 5 cc of alcohol and 2 drops of corallin indicator to the solution. Titrate to neutrality with acid or alkali as required, and add 25 cc of 2 N sodium sulfite solution. Let the mixture stand for 10 minutes, and titrate with N H_2SO_4. Run a determination on a blank. Derive the formula for the calculation of grams of CH_2O per 100 cc of solution.

TEST METHOD 3

RESIN CONTENT OF SOLUTIONS

Weigh out approximately 10 grams of solution into a weighed, suitable flat-bottomed metal container, such as an aluminum milk dish, a can cover, or an ointment can. Remove the volatile material by evaporating the solution under a hood at 150° C on a steam or electric hot plate, using caution to prevent foaming, etc., which may result in a loss of material. Allow the container to remain on the hot plate to a constant weight or for about 1 to 2 hours after *all the volatile material has evaporated.*

Record Data

Wt. container + solution ....
Wt. container ....
Wt. solution ....

Wt. container + dry resin ....
Wt. container ....
Wt. resin ....

$$\% \text{ Resin} = \frac{\text{Wt. resin}}{\text{Wt. solution}} \times 100.$$

TEST METHOD 4

STROKE CURE

The stroke cure is the time required for a resin to convert from a fusible or liquid condition at a definite temperature while being stroked with a spatula to a condition at which the spatula either no longer sticks to the resin or slides over it with relative ease.

The test is conducted on a suitable heated steel plate about 6 by 6 inches square, so arranged that it can be heated variably from 100 to 300° C. Electrically, this may be done with a rheostat. A source of high-pressure steam controlled by a reducing valve is also suitable. The temperature of the plate is observed with a thermocouple or with a thermometer inserted in a well drilled in the plate. The time is noted with a stop watch or other timing devices reading in minutes and seconds. The spatula blade should be about 4 inches long and about one-half inch wide. The removal of the resin from the hot plate is readily accomplished by means of a scraper or a putty knife after the resin is fully cured. For comparable results it is essential that the same amount of varnish be delivered by means of a kitchen measuring spoon of about 2- to 4-cc capacity. Powdered resins are usually weighed out to approximately 1 gram.

The area over which the resin or varnish is spread during the test likewise affects the values obtained, and an effort should be made to spread the resin or varnish over the same area each time the test is conducted.

Procedure for Varnishes

Adjust the hot plate to the temperature required. Transfer the measured amount of varnish or resin solution to the center of the hot plate, start the stop watch, and spread the varnish over an area of about 7 square inches. Keeping the spatula flat, stroke the spread varnish longitudinally and parallel to the surface of the hot plate, using approximately 90 to 100 strokes per minute. Alternate the strokes progressively from one edge of the resin to the other. Note and record the time for all the solvent or volatile to evaporate or dry, time for the resin to string, time of cure, color of resin, and the type of cure, e.g., hard, rubbery, soft. Use 150° C for phenolic varnishes and about 130° C for urea syrups unless otherwise specified. Allow the resin to remain on hot plate for another minute or two, and remove with putty knife or scraper.

Sample	*Time for Evaporation*	*Time to String*	*Time Cure*	*Cure Color*	*Cure Type*
....	....	....	....	....	....
....	....	....	....	....	....

Procedure for Resins

Substantially the same procedure is used for resins as for varnishes except that approximately 1 gram of powdered resin is used and is spread over an area of about 3 square inches. As a rule these resins are more viscous, and about 75 to 85 strokes per minute are needed. The time for the resin to melt is also recorded.

Sample Number	*Time to Melt*	*Time to String*	*Time to Cure*	*Cure Color*	*Cure Type*
....	....	....	....	....	....
....	....	....	....	....	....

TEST METHOD 5

REFRACTIVE INDEX

Any standard refractometer maintained at a constant temperature may be used for this test. The measurement is made at 25° C. If the refractive index is used in conjunction with another determination, both measurements should be made at the same temperature. Resin solutions should not be used in the refractometer until a solvent is known which is inert toward the prism cement and is effective in removing the resin from the prism.

TEST METHOD 6

SPECIFIC GRAVITY OF VARNISHES AND LIQUIDS

Method A. Westphal Balance

The standard Westphal balance may be used, since it is more accurate than hydrometers. For most industrial applications, however, hydrometers are sufficiently accurate.

Method B. Hydrometer Method

A uniform, well-stirred sample of varnish is poured into a hydrometer jar, or any suitable glass tube of sufficient depth, to within 1 to one-half inches from the top of the jar. Immerse a thermometer in the jar, and with constant stirring adjust the temperature of the varnish to 25° C, or to whatever temperature is desired or specified on the hydrometer. This adjustment may be made by immersing the jar to below the level of the varnish, in a constant temperature bath, or in a bath of cool running water. If a bath of cool running water is used, remove jar from cooling bath; otherwise leave the jar in the constant temperature bath. Carefully insert a *clean and dry hydrometer* into the solution, permitting it to sink into the varnish very slowly and of its own accord.

Varnishes of high resin content or of very high viscosity may tend to form a skin on their surfaces. This skin will tend either to hold up the hydrometer or to anchor it in place in the varnish. This may be eliminated by slowly tilting the jar backward and forward. Bubbles of air may adhere to the sides of the hydrometer, resulting in inaccurate data. Either allow sufficient time for these bubbles to rise to the surface or tilt the jar slowly to eliminate them.

Record the reading at the level of the varnish as the gravity of the varnish. If these values are to be used in conjunction with other tests, all measurements should be made at the same temperature.

TEST METHOD 7

VISCOSITY DETERMINATION

This method outlines the determination of the absolute viscosity of a liquid by measuring the time of flow of a definite volume of liquid through a calibrated Ostwald viscometer as modified by Cannon and Fenske.

Procedure

Pipette 10 ml of the liquid whose viscosity is to be determined into the larger arm of the calibrated viscometer, which has been clamped into a constant temperature bath at 25 ± 0.1° C or other specific temperature. By means of a length of rubber tubing attached to the smaller arm, suck the liquid over the upper mark on the smaller arm. Remove the suction, and start the timer or stop watch as the liquid level passes the upper mark. Stop the timer as the liquid level passes the lower mark. Repeat until the time readings check each other within 0.2 second. The lower limit of time is 40 seconds.

Calculation for Viscosity in Centipoises

$$\text{Viscosity in centipoises} = K \cdot S \cdot t$$

where K = viscometer constant,
S = specific gravity of liquid at 25° C or other specified temperature,
t = time in seconds for the liquid to flow between marks.

Calibration of a Viscometer

Viscometers may be calibrated at a specific temperature in two ways, by using a liquid whose viscosity and specific gravity at the specific temperature are known or by using a liquid whose time of flow in a calibrated viscometer is known.

(*a*) With a liquid of known viscosity and specific gravity, the K of the viscometer is given by the expression:

$$K = \frac{N}{St}$$

where K = calibration constant for the viscometer,
S = specific gravity,
t = time of flow in seconds,
N = viscosity in centipoises of the liquid at the specified temperature.

(*b*) With another calibrated viscometer, the K of the viscometer is given by the following formula:

$$\frac{K_a t_a}{t} = K$$

where K = calibration constant for the viscometer,
K_a = constant of the previously calibrated viscometer,
t_a = time of flow in seconds of the liquid in the calibrated viscometer,
t = time of flow in seconds of the liquid in the viscometer being calibrated.

In both cases, the determinations should be made at a specified temperature. Care should be taken to maintain the temperature as constant as possible since a change of 0.1° C will change the viscosity by about 1%. The time of a flow should be over 40 seconds in all cases; otherwise turbulent flow instead of laminar flow conditions will result.

TEST METHOD 8

*p*H OF RESIN SOLUTIONS

Any standard method of determining *p*H may be used whenever the color of the solution is not a factor. Accurate and convenient determinations are best obtained by using glass electrodes. Standard *p*H meters may be purchased complete and ready to operate. Each student using the instrument is required *to read and understand thoroughly* the instructions accompanying the instrument. The following precautions must also be followed:

1. Never determine the *p*H of a resin solution until a solvent which is inert toward the electrodes and effective for dissolving the resin has been determined.

2. Never allow the resinous materials to dry on the electrodes or to remain there longer than necessary.
3. Wash the electrode thoroughly with solvent after use, in a series of solvents, if necessary, to arrive at final washings with distilled water.
4. Never allow the electrodes to dry, but treat or immerse them to keep them wet as instructed by the manufacturer of the instrument.

TEST METHOD 9

PRECIPITABILITY

This test consists in determining the amount of precipitant required to precipitate the resin from a specified solution. Since water is the most abundant solvent, and likewise lowest in cost, this test deals with the amount of distilled water necessary to cause the initial precipitation of a resin from its solution, whose solvent is soluble in or compatible with water. Since the solubility of some resins changes considerably with temperature, all determinations should be made at the same temperature, and the temperature of the resin solution and the water used should be within 0.5° C of each other.

Procedure

By means of a syringe or a pipette having a rather large opening, introduce 5 cc of the resin solution or varnish into a clean 50-cc Erlenmeyer flask. Add distilled water from a burette, as in titration experiments, while continually stirring the solution. The volume of water in cubic centimeters required to produce a cloudiness which persists for at least 2 minutes is recorded as the precipitability point. If precipitation does not occur on the addition of 40 cc of water, then the precipitability is expressed as infinite. Record the data as follows:

Cubic centimeters of resin solution ....

Cubic centimeters of water ....

$$\frac{\text{Cubic centimeters of water}}{\text{Cubic centimeters of resin solution}} = \text{Precipitability}$$

TEST METHOD 10

ACETONE SOLUBILITY

This method outlines the determination of the acetone solubility of a resin solution as a means of determining the rate of cure or polymerization of the resins whose intermediate stages are acetone soluble. For the purposes of this method, the following definitions have been used:

Varnish deposit = Increase in weight by impregnation (after drying loss of solvent for 5 minutes at 100° C)

Varnish = Uncured resin plus solvent

Volatile loss = Loss of solvent from deposit on the impregnated material on heating

Procedure

Cut out and weigh a 10 by 8 inch sheet (or other suitable size) of the paper or fabric to be impregnated. Impregnate uniformly with varnish solution to 50 ± 5% varnish deposit. Allow the impregnated sheet to air-dry for 15 minutes. Then determine the exact percentage of deposit by drying the impregnated sheet in an air-circulating oven for 5 minutes at 100° C. Cool in a desiccator and weigh. Record the data as follows:

X = Weight of sheet and deposit ....
Y = Weight of sheet ....
Z = Weight of deposit ....

$$\% \text{ Varnish deposit} = \frac{Z \times 100}{X}$$

The center section, 6 by 5½ inches, of the sheet is selected by trimming the edges with a paper cutter. Cut this center section into five strips 1 by 6 inches long. Punch a hole in one end of each strip. Identify them as strips 0, 1, 2, 3, and 4. Weigh the numbered strips. Call this weight A.

Immerse strip 0 in a beaker of acetone for 10 minutes, dry for 5 minutes at 120° C, cool in a desiccator, and weigh. Calculate the percentage of varnish deposit as follows:

$$\% \text{ Varnish deposit} = 100 \times \frac{A - \text{Weight of dried strip 0 after acetone extraction}}{A}$$

This value should equal within experimental error the value of % varnish deposit obtained above.

Now hang strips 1, 2, 3, and 4 in the 120° C oven for 5, 15, 30, and 45 minutes, respectively. Remove each strip quickly at its proper time, and cool in the desiccator for 5 minutes. Weigh each strip, and record this weight as B. The difference between A and B represents the volatile loss.

Immerse the four strips in acetone for 10 minutes; dry at 120° C for 5 minutes. Cool in a desiccator and weigh. Record this weight as C. This weight is the weight of the sheet plus the cured (non-acetone extractable) resin.

The percentage of acetone solubility corrected for volatile loss is calculated as follows:

$$\% \text{ Acetone solubility} = \frac{100(B - C)}{\% \text{ Varnish deposit} \times A - (A - B)}$$

Record data in the following table:

Strip	*Time Cured, Minutes*	*A*	*B*	*C*	*% Acetone Solubility*
0	0	......	......	......	....
1	5	......	......	......	....
2	15	......	......	......	....
3	30	......	......	......	....
4	45	......	......	......	....

Plot the time cured at 120° C versus % acetone solubility to obtain the cure characteristics of the specific resin.

TEST METHOD 11

RESIN CONTENT AND VOLATILE CONTENT OF LAMINATED STOCK

Resin Content of Laminated Stock

Cut out and record the weight of a 6 by 6 inch sheet (A) of untreated paper or cloth corresponding to the material to be impregnated. Record the weight of a similar-sized sheet (B) which has been impregnated with resin and dried, ready for use as a laminated stock. The difference in weights represents the weight of varnish deposit. (See Method 10 for definition.)

The volatile material is determined by heating the impregnated sheet B at 150° C for 15 minutes, or to constant weight, and recording weight as (C).

Record as follows:

	Weight
Sheet A	....
Sheet B	....
Sheet C	....

Calculations where R = % Varnish deposit:

$$V = \%\ \text{Volatile loss}$$

$$R + V = \frac{B - A}{B} \times 100$$

$$R = \frac{C - A}{B} \times 100$$

$$V = \frac{B - C}{B} \times 100$$

TEST METHOD 12

DETERMINATION OF FLOW POINT OF RESINS

Part A. Melting-Point Method

This method, used industrially as a control measure, requires considerable experience and time to perform accurately. It is included as a general disclosure for those who care to develop the technique. Actually, thermocouples inserted in steel rods are used instead of thermometers. For student study the regular capillary tube melting-point method is recommended. Since many of the resins do not truly melt and become fluid, a certain amount of judgment must be used by the student in deciding the "end point," or the "melting point."

Part B. Industrial Method

1. Bulb Method. The bulb, about 1 inch long, of a straight barrel thermometer is coated uniformly with 0.05 inch of powdered resin. The thermometer is previously heated sufficiently to cause the resin to soften and adhere to the bulb. This is achieved by spreading the resin on a smooth, flat surface. The bulb of the thermometer is then rolled over it, rolling-pin fashion, until the desired thickness, as measured by a micrometer, is obtained. The thermometer is then mounted in a 1-inch test tube, which acts as an air bath. This test tube is calibrated with a zero mark, about 1 to 2 inches from the bottom of the tube and a 0.2-inch mark below the zero mark. The end of the thermometer bulb is adjusted to the zero level of the test tube. This tube is then heated in a suitable clear liquid bath, raising the temperature at the rate of 2 to 3° C per minute. The air-bath temperature will lag 10 to 15° C behind the liquid-bath temperature. The temperature at which the resin flows from zero level to the 0.2-inch level is recorded as the flow point of the resin.

2. Sliding-Bar Method. For details of this method, consult *Journal of the American Chemical Society,* Volume 52, page 3128 (1930).

TEST METHOD 13

WATER ABSORPTION OF MOLDED COMPOUNDS

A.S.T.M. methods should be followed whenever possible, but since many laboratories cannot afford the required molds any suitable molded piece may be used for general data. When comparative results are to be obtained, however, specimens must be of comparable dimensions. Weigh the molded sample as received.

If the specimen is thermoplastic, dry it in an oven for 24 hours at 50 ± 3° C over anhydrous calcium chloride.

Thermosetting specimens are dried in an oven for 24 hours at 105 to 110° C to remove water and other volatiles. Cool the dried sample in a desiccator, and reweigh.

Immerse the sample wholly in a suitable container of distilled water and maintain the temperature at 25 ± 2° C. At the end of 24 hours, remove the sample from the water, and wipe off all surface water with a dry cloth. Weigh the specimen immediately, and replace it in the water. After 24 more hours of immersion, wipe, and weigh again. The calculations are based on the dry weight.

Data

Original Wt. Sample	*Dry Wt. Sample*	*Weight Sample, 24 Hours Immersion*	*Weight Sample, 48 Hours Immersion*
....	....	....	....

% Volatile in Original Sample	*% Water Absorbed, 24 Hours*	*% Water Absorbed, 48 Hours*
....	....	....

TEST METHOD 14

BOILING-WATER TEST

After weighing the molded sample, immerse it in boiling water for 15 minutes, followed by immersion in cold water for 5 minutes. Remove the sample from the cold water, wipe off all surface water with a dry cloth, and weigh immediately. Repeat the boiling and cooling cycle, recording the weight after each cycle. Continue the cycle either until 10% of the water is absorbed or for 10 cycles, whichever occurs first. Report the dimensions of the molded sample before and after the boiling cycle.

For comparative value with other samples, plot the percentage of water absorption against the number of cycles. Record data as follows:

		Dimensions		
Cycle	*Weight Original Sample*	*Before Boiling*	*After Boiling*	*Water Absorption*
1	....	....	....	....
2	....	....	....	....
3	....	....	....	....
4	....	....	....	....
5	....	....	....	....
6	....	....	....	....
7	....	....	....	....
8	....	....	....	....
9	....	....	....	....
10	....	....	....	....

TEST METHOD 15

SPECIFIC GRAVITY OF MOLDED PARTS

Two methods are suggested and, where extreme accuracy is not needed, Method *A* is recommended for the ease and rapidity with which it is performed. In either method, mold samples that are affected by the solvent cannot be used. In that case, the general principles may be applied, using suitable liquid media.

An effort should be made to maintain close control over temperature in the methods described below since in many cases the gravity changes are high with relatively small changes in temperature.

Method A. Using Solutions of Known Gravity

1. Using distilled carbon tetrachloride, whose specific gravity is approximately 1.59, and distilled benzene of a specific gravity of 0.86, prepare suitable mixtures of the two to obtain a series of solutions having specific gravities over the range desired, e.g., 1.1, 1.2, 1.3, 1.35, 1.38, and 1.41. Check the specific gravity of these solutions either with a hydrometer or with a Westphal balance. Label each solution with its tested specific gravity. To test the gravity of the sample, immerse the sample in a solution, roughly estimated to be equal to the gravity of the sample. If the sample sinks, it should be tested in a solution of higher gravity; if it floats, in a solution of lower gravity. If necessary, prepare a solution intermediate to those already prepared, and take as the specific gravity, the gravity of the solution in which the sample just sinks. Recheck the density of the solution to determine if any change in density has occurred during the determination, either by evaporation or by dilution, as when a sample is transferred from one solution to another. Keep the solutions tightly covered when not in use, and always recheck their gravities before reuse.

2. Alternately, aqueous zinc chloride solutions of known gravity may likewise be used in place of the organic mixtures. Another procedure utilizes high-gravity zinc chloride solutions which are titrated with water until the sample to be tested just sinks in the solution. A hydrometer is then used to determine the density of the solution.

Method B. Weighing Method

Weigh a sample to be tested that can be immersed freely in a 150-cc beaker and record this weight as WA. Fasten a length of copper wire to the sample, the length of the wire being sufficient to permit proper immersion in the beaker when the other looped end is attached to the stirrup holder of the balance.

Weigh the wire and sample in air. Record this weight as S. The weight of the wire in air is $S - WA$, which is recorded as A.

Place the sample with the copper wire attached to it in the 150-cc beaker, containing enough distilled water for the complete submersion of the sample. Cool the water and sample to 25° C or to any other desired temperature. Place the small wooden bridge provided with the balance over the left balance pan and the beaker containing water and sample on this bridge. Suspend the sample by means of the looped copper wire from the stirrup holder of the balance. The wire and sample are now weighed while the sample and part of the wire are submerged in water. Let this weight be known as X. With a pair of shears cut off the copper suspension wire at the surface of the water while the balance is in equilibrium. The sample, plus a short part of the wire, falls to the bottom of the beaker. The greater portion of the suspending wire remains hanging from the stirrup of the balance. Remove the beaker and bridge from the balance, and weigh the suspended portion of wire. Let this weight be known as Y.

The specific gravity is determined as follows:

1. The weight of the portion of the suspending wire which was immersed in water is determined by subtracting from the total weight of the suspending wire the weight of that portion which was cut off and remained suspended on the stirrup of the balance. Expressed in formula, it is $A - Y$. Let this weight be known as Z.

2. Compute the apparent weight R of the submerged wire as follows, using 8.90 approximately as the specific gravity of the copper.

$$R = \frac{(\text{Sp. gr. of copper} - \text{Sp. gr. of water}) \cdot X \cdot Z}{\text{Sp. gr. of copper, 8.90}}$$

3. The weight of the sample in water is equal to $(S - Y) - R$. Let the result be known as WW. Specific gravity of the sample is equal to the weight of the sample in

air, divided by the weight of the sample in air minus the weight of the sample in water. Calculate the specific gravity using the formula:

$$\frac{WA}{WA - WW} = \text{Specific gravity}$$

If a very fine wire is used, results accurate enough for all practical purposes can be obtained by neglecting the weight of the wire. This is especially true if the sample is quite large.

Record data as follows:

Designation	*Weight*
WA	....
S	....
A	....
X	....
Y	....
Z	....
R	....
WW	....

TEST METHOD 16

OIL SOLUBILITY

Place 10 grams of oil in a small beaker and heat over a free flame, with continued stirring until the temperature of oil reaches 210° C. With stirring, add 5 grams of finely ground resin.

Note if resin goes into solution. Allow to cool, and note if resin precipitates. Report the resin as oil soluble or oil insoluble, both hot and cold.

TEST METHOD 17

SOLVENT SOLUBILITY

Introduce 1 gram of finely ground resin in 5 cc of cold solvent in a suitable test tube. Stir thoroughly with a glass rod, and report results as follows: completely soluble (*CS*); partially soluble (*PS*); insoluble (*IS*).

TEST METHOD 18

GELATION TIME OF OILS

Introduce a 1-inch layer of oil in a 50-cc beaker or any other suitable metal or glass container, and heat rapidly without burning to about 280° C. Maintain at that temperature until gelation occurs.

Use a thermometer to effect gentle stirring, recording the gelation after the time required to reach 280° C. If comparative results are to be obtained among a series of samples, the rate of heating and the volume of oil used should be comparable. If the gelation of oils is studied in the presence of resins, the resins should be added in powdered form after the oil has reached the required temperature.

TEST METHOD 19

ACID NUMBER OF ALKYD RESINS

Preparation of Alkali Blue Indicator

Dissolve 0.2 gram of alkali blue in 100 cc of 50% aqueous 95% alcohol.

Part I. Determination for a Soft Resin

Weigh a 6-inch glass stirring rod accurately and then pick up 1 to 2 grams of soft resin on one end of the rod. Weigh again, and calculate the exact weight of the resin taken. Put the stirring rod with the resin in a 250-cc Erlenmeyer flask. Add 75 cc of acetone, and stir until the resin is dissolved. Add alkali blue solution, and titrate to a red end point with 1.0 *N* KOH solution. Run a blank on the solvent, include correction in calculations, and record data as follows:

Weight of sample ....

Volume of .... *N* alkali for sample + solvent

Volume of .... *N* alkali for solvent (blank)

Volume of .... *N* alkali for sample

Acid number ....

Part II. Determination for a Hard Brittle Resin

Powder 1 to 2 grams of the alkyd resin and weigh directly into a 250-cc Erlenmeyer flask. Dissolve in 75 cc of acetone, and treat as in Part I.

Calculations

Express the acid number as the number of milligrams of KOH to neutralize 1 gram of sample:

$$\text{Acid number} = \frac{\text{Cubic centimeters of alkali for sample} \times N \text{ alkali} \times 56.11}{\text{Weight of sample in grams}}$$

TEST METHOD 20

GELATION OF ALKYD RESINS

Follow the general procedure under Test Method 18, using the same or a higher or lower gelation temperature if necessary to distinguish among a series of samples.

TEST METHOD 21

DETERMINATION OF UNSATURATION

This method covers the determination of the amount of unsaturation in monomers, or monomer-polymer mixtures. It is also applicable to drying oils, alkyd resins, etc.

Reagents

$0.5\ N$ bromine solution in chloroform.
$0.1\ N$ sodium thiosulfate solution.
Starch solution (1 gram of soluble starch in 200 ml of water).
40% potassium iodide solution.

Procedure

Weigh 2 grams of the material into a 250-ml wide-mouthed Erlenmeyer flask. Titrate with the bromine-chloroform solution, keeping the contents of the flask cooled with ice water. Add the bromine solution until the color of the mixture in the flask no longer fades. Then add one-third more of the bromine solution. Let the solution stand for 5 minutes in the ice water, with frequent shaking. Add 10 ml of 40% potassium iodide solution, and titrate the freed iodine with $0.1\ N$ sodium thiosulfate, using starch solution near the end point. Shake well during titration.

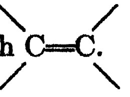
The bromine solution is standardized by adding 10 ml of 40% potassium iodide solution to 5 ml of the bromine solution as run out of the burette. (Do not pipette the bromine-chloroform solution!)

Titrate the iodine freed with $0.1\ N$ sodium thiosulfate solution, using starch solution near the end point. The normality of the bromine solution is calculated as follows:

$$N = \frac{N_t V_t}{V}$$

where N = normality of bromine solution,
V = volume of bromine solution taken,
N_t = normality of thiosulfate solution,
V_t = volume of thiosulfate solution.

Calculation of Unsaturation

One mole of bromine adds to each .

$$\frac{(NV - N_tV_t)M}{10 \times W \times 2 \times D} = \%\ \text{Unsaturation}$$

where N = normality of bromine solution,
V = volume of bromine taken,
N_t = normality of thiosulfate solution,
V_t = volume of thiosulfate used to back-titrate,
W = weight of sample,
M = molecular weight of the monomer or corresponding monomer,
D = number of aliphatic double bonds per mole of corresponding monomer, e.g., in styrene $D = 1$, in divinylbenzene $D = 2$, etc.

TEST METHOD 22

POLYVINYLFORMAL

Weigh out accurately a 2- to 5-gram sample of the reaction solution into a 50-cc Erlenmeyer flask. Spread the resin in a film over the glass surface of the walls of the flask, and add 25 cc of distilled water. Break the resin up and wash it well with the water. Filter, and collect filtrate. Wash the resin in the flask and on the filter with two more washes of 25 cc of warm water each, crushing the resin into fine particles and using all other precautions to wash it thoroughly. Save and combine all filtrates. This procedure washes substantially all the acetic acid and formaldehyde from the resin.

To the filtrate add 3 drops phenolphthalein indicator and warm to 67° C. Titrate with N NaOH, and record that titration. Add 10 to 15 cc excess of N NaOH, and then add 10 to 15 cc of a one to four dilution of perhydrol in water. Let stand for one-half hour, and then boil to destroy excess H_2O_2. Add 3 more drops of phenolphthalein. Over-titrate the end point with N H_2SO_4, and then back-titrate to the end point with N NaOH. Correct the results by running the same determinations on a blank.

Record data as follows:

Wt. sample ....

a = Cubic centimeters × N NaOH for filtrate ....

b = Cubic centimeters × N NaOH excess ....

c = Cubic centimeters × N H_2SO_4 to over-titrate ....

d = Cubic centimeters × N NaOH to back-titrate ....

Calculate as follows:

1. Acetic acid:

$$\frac{a \times 60}{1000 \times \text{Weight of sample}} = \text{Grams of acetic acid per gram of sample}$$

2. Formaldehyde:

$$\frac{(b + d - c) \times 30}{1000 \times \text{Weight of sample}} = \text{Grams of formaldehyde per gram of sample}$$

TEST METHOD 23

ACETYL GROUPS

In a ground-glass flask, fitted with a reflux condenser, place an accurately weighed sample of 1 to 1.5 grams of the material to be tested. Dissolve the sample in 25 to 30 cc of freshly distilled pyridine. Add between 10 and 15 cc of 0.5 N KOH aqueous solution. Reflux 1 to 1½ hours on a suitable bath. Cool to room temperature, add phenolphthalein, and over-titrate the end point with 0.5 N HCl. Back-titrate with 0.1N KOH.

Calculation

In calculation: 1 mole KOH used = 1 mole acetyl groups.

TEST METHOD 24

HYDROXYL GROUPS

In a ground-glass acetylation flask place approximately a 1-gram sample and dissolve in 25 to 30 cc of redistilled pyridine. Add ½ cc of redistilled acetic anhydride. Heat for one-half hour at 115° C. Wash the condenser with 5 cc of pyridine, and titrate the reaction mixture for residual acetic anhydride, using 0.5 N KOH with phenolphthalein as indicator.

Run a blank on acetic anhydride and pyridine refluxed in the same manner and introduce the correction in the calculations.

Calculations

In calculations: One acetyl group is equivalent to one hydroxyl group.

TEST METHOD 25

FORMAL GROUPS

In a 1-liter round-bottomed flask arranged for steam distillation place approximately 2 grams of resin. Add 250 cc of a one to one mixture of 85% phosphoric acid and water. Steam-distill the mixture, collecting 500 cc of distillate.

Determine the formaldehyde content of the distillate, and calculate the percentage of formalization of the sample.

TEST METHOD 26

DETERMINATION OF ACID NUMBER

Indicators

Phenolphthalein solution is prepared by dissolving 1 gram of phenolphthalein in 100 cc of 95% ethyl alcohol. Alkali blue solution is prepared by dissolving 0.2 gram of alkali blue in 100 cc of 50% aqueous ethyl alcohol.

Part I. Rosin Determination

Dissolve 2 grams of powdered rosin in 50 cc of 95% ethyl alcohol in a 250-cc Erlenmeyer flask, using heat if necessary. Cool to room temperature, and, using phenolphthalein as an indicator, titrate with 3 *N* NaOH.

If rosin solution is rather dark in color, use alkali blue as the indicator, titrating to a red end point. Run a blank on the solvent, and make correction in the calculation.

Part II. Limed Rosin Determination

To 50 cc of benzene in a 250-cc Erlenmeyer flask, add 1 gram of powder-limed rosin, and allow as much of it as possible to dissolve. Add 50 cc of 95% alcohol to dissolve the remainder of the material. Titrate as in Part I, including the correction for the solvent.

Part III. Ester Gum Determination

Dissolve 2 grams of powdered ester in 50 cc of benzene and 50 cc of 95% alcohol in a 250-cc Erlenmeyer flask. Titrate as in Part I, including the correction for the solvent.

Refer to Test Method 19 for the method of calculation.

TEST METHOD 27

MOISTURE CONTENT OF MOLDING COMPOUNDS

On a triple-beam balance weigh out 50 grams to the nearest 0.01 gram of material and place it in a 250-cc Erlenmeyer flask. Add 150 cc of water-saturated benzene and attach the flask to a Stark and Dean trap attached to a reflux condenser. Adjust the heat so that reflux occurs and the condensate drips into the Stark and Dean tube at the rate of 2 to 5 drops per second. Reflux for about one hour or until no more water distills into the trap.

$$\%\ \text{Water in sample} = \frac{\text{Volume of water in trap}}{\text{Weight of sample}} \times 100$$

APPENDIX

A list of industrial sources of supplies suitable for use in the experiments of this manual has been appended for the purpose of assisting those laboratories that require relatively large amounts of material in their work. When small quantities of the materials are required, they should be purchased from established sources.

No attempt has been made to give a complete list of suppliers. Nor is this list to be considered an endorsement by the author either of the suppliers or of their materials. The manufacturers listed have supplied the author and his associates with satisfactory products in the past.

Wartime conditions may make it impossible to obtain some of the materials needed for these experiments. Other sources of supply should be investigated, such as are listed in: (1) *Chemical Industries Buyers' Guide Book Number*, 17th Annual Revision, 1942–1943, Vol. 51, No. 5, October, 1942, Tradepress Publishing Corp., Inc., 522 Fifth Ave., New York, N. Y., or 309 West Jackson Blvd., Chicago, Ill. (2) *Chemical Engineering Catalogue*, Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y.

The raw materials are listed in the order in which they are first used in the experiments, and therefore may not be listed in the experiment under study.

Experiment	*Material*	*Sources*
1	Phenol	The Barrett Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y. The Dow Chemical Co., Midland, Mich. The Monsanto Chemical Co., Merrimac Chemical Division, Everett Station, Boston, Mass., or 1700 S. Second St., St. Louis, Mo. Reilley Tar & Chemical Corp., 1615 Merchants Bank Bldg., Indianapolis, Ind.
2	Formalin and Paraformaldehyde	E. I. du Pont de Nemours & Co., Inc., Grasselli Chemical Dept., Wilmington, Del. Heyden Chemical Corp., 50 Union Square, New York, N. Y. American Cyanamid & Chemicals Corp., 30 Rockefeller Plaza, New York, N. Y.
	Trioxane	E. I. du Pont de Nemours & Co., Inc., Grasselli Chemical Dept., Wilmington, Del.
	Hydroxylamine Hydrochloride	J. T. Baker Chemicals Co., N. Broad St., Phillipsburg, N. J. Eastman Kodak Co., 343 State St., Rochester, N. Y.
5	Hexamethylenetetramine	E. I. du Pont de Nemours & Co., Inc., Electrochemicals Dept., Wilmington, Del. Heyden Chemical Corp., 50 Union Square, New York, N. Y.
	Bis-phenol-A	Dow Chemical Co., Midland, Mich.
6	Resin Flask	Ace Glass, Inc., Vineland, N. J. Catalogue 6945. Vacuum distilling apparatus. Pyrex glass. Dome should have 3 necks. Scientific Glass Apparatus Co., Bloomfield, N. J. Catalogue J1762. Resin flask, 3-necked, Pyrex glass.
7	Cresols and Xylenols	The Barrett Division, The Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y. Reilley Tar & Chemical Corp., Merchants Bank Bldg., Indianapolis, Ind.
8	Resorcinol	Pennsylvania Salt Mfg. Co., 1000 Widener Bldg., Philadelphia, Pa.
	1,3,5-Xylenol	See Experiment 7. Also, Shell Chemical Co., San Francisco, Calif.
	Casting Resin Dyes	National Aniline Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y. Calco Dye Division, American Cyanamid Co., Bound Brook, N. J. E. I. du Pont de Nemours & Co., Inc., Organic Chemicals Dept., Wilmington, Del.

Experiment	*Material*	*Sources*
11	Paper *A*—No. 701	Hurlburt Paper Co., Main St., S. Lee, Mass.
	Paper *B*—Bleached Kraft—0.007 to 0.010 inch	Rayonier, Inc., 343 Sansome St., San Francisco, Calif.
		Hollingsworth & Whitney Co., 60 Batterymarch St., Boston, Mass.
		Nekoosa Edwards Paper Co., Port Edwards, Wis.
		St. Regis Paper Corp., 230 Park Ave., New York, N. Y.
12	Laminating Press	Watson Stillman Co., 118 Aldene Rd., Roselle, N. J.
		Charles F. Elms Engineering Works, 225 N. Morgan St., Chicago, Ill.
		Hydraulic Press Manufacturing Co., Mount Gilead, Ohio.
	N.E.M.A.—Laminated Phenolic Products Standards	National Electrical Manufacturers Assoc., 155 East 44th St., New York, N. Y.
	A.S.T.M. Standards	American Society for Testing Materials, 260 South Broad St., Philadelphia, Pa.
13	Butylphenol	Dow Chemical Co., Midland, Mich.
	Arylphenol	Dow Chemical Co., Midland, Mich.
		Sharples Chemicals Inc., 23rd and Westmoreland Sts., Philadelphia, Pa.
14	Calcium Stearate	American Cyanamid & Chemicals Corp., 30 Rockefeller Plaza, New York, N. Y.
		Metasap Chemical Co., Logan and Davis Sts., Harrison, N. J.
15	Wood Flour	E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. (Grade 109.)
		Wood Flour, Inc., Winchester, N. H. (Grade 3A.)
	Asbestos	Johns-Manville Corp., 22 E. 40th St., New York, N. Y.
	Cotton Flock	Rayon Processing Co., 86 Tremont St., Central Falls, R. I.
	Chopped Fabrics	Claremont Waste Manufacturing Co., Claremont, N. H.
	Dyes	Kohnstamn & Co., Inc., Philadelphia, Pa.
		General Dyestuff, 435 Hudson St., New York, N. Y.
16	Molding Press	See Experiment 12.
17	Furfural	Quaker Oats Co., 141 W. Jackson Blvd., Chicago, Ill.
18	*Tert*-Amylphenol	Sharples Chemicals, Inc., 23rd and Westmoreland Sts., Philadelphia, Pa.
		Dow Chemical Co., Midland, Mich.
	Styrene	Dow Chemical Co., Midland, Mich.
19	Butylphenol	Dow Chemical Co., Midland, Mich.
	Phenylphenol	Dow Chemical Co., Midland, Mich.
20	Oiticica Oil	Brazil Oiticica, Inc., New York, N. Y.
		W. R. Grace & Co., New York, N. Y.
		Murray Oil Products Co., Philadelphia, Pa.
	Tung Oil	Werner G. Smith Co., Division of Archer-Daniels-Midland Co., 2191 W. 110th St., Cleveland, Ohio.
		Harshaw Chemicals Co., 1945 E. 97th St., Cleveland, Ohio.
		Spencer Kellogg & Sons, Inc., 100 Delaware Ave., Buffalo, N. Y.
	Linseed Oil	Harshaw Chemicals Co., 1945 E. 97th St., Cleveland, Ohio.
		Archer-Daniels-Midland Co., Minneapolis, Minn.
		Spencer Kellogg & Sons, Inc., 100 Delaware Ave., Buffalo, N. Y.
	Perilla Oil	Werner G. Smith Co., Division of Archer-Daniels-Midland Co., 2191 W. 110th St., Cleveland, Ohio.
	Castor Oil	The Baker Castor Oil Co., 120 Broadway, New York, N. Y.
21	Driers	Harshaw Chemicals Co., 1945 E. 97th St., Cleveland, Ohio.
22	Urea and Dimethylolurea	E. I. du Pont de Nemours & Co., Inc., Ammonia Dept., Wilmington, Del.
	Chloroacetamide	Dow Chemical Co., Midland, Mich.
24	Thiourea	American Cyanamid & Chemicals Corp., 30 Rockefeller Plaza, New York, N. Y.
		Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.

Experiment	*Material*	*Sources*
25	Melamine	American Cyanamid & Chemicals Corp., 30 Rockefeller Plaza, New York, N. Y.
		Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.
26	Alpha Flock	Brown Co., 500 Fifth Ave., New York, N. Y.
31	Stark and Dean Apparatus	Ace Glass, Inc., Vineland, N. J.
		Scientific Glass Apparatus Co., Bloomfield, N. J.
33	Phthalic Anhydride	Monsanto Chemical Co., Merrimac Chemical Division, Everett Station, Boston, Mass.
		National Aniline Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.
		The Barrett Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.
		American Cyanamid & Chemicals Corp., 30 Rockefeller Plaza, New York, N. Y.
	Maleic Anhydride	National Aniline Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.
		American Cyanamid & Chemical Corp., 30 Rockefeller Plaza, New York, N. Y.
		The Barrett Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.
		Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y.
	Succinic Acid	National Aniline Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.
	Diethylene Glycol	Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y.
		Dow Chemical Co., Midland, Mich.
34	Linseed-Oil Fatty Acid	Spencer Kellogg & Sons, Inc., 100 Delaware Ave., Buffalo, N. Y.
	Tung Oil Fatty Acid	Werner G. Smith Co., Division of Archer-Daniels-Midland Co., 2191 W. 110th St., Cleveland, Ohio.
	Castor-Oil Acids	The Baker Castor Oil Co., 120 Broadway, New York, N. Y.
39	Benzoyl Peroxide	Lucidol Corp., Buffalo, N. Y.
	Naphthenate Driers	Harshaw Chemicals Co., 1945 E. 97th St., Cleveland, Ohio.
40	Styrene	Dow Chemical Co., Midland, Mich.
41	Polyvinyl Alcohol	E. I. du Pont de Nemours & Co., Inc., Electrochemicals Division, Wilmington, Del.
		Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y.
	Aerosol OT	American Cyanamid & Chemicals Corp., 30 Rockefeller Plaza, New York, N. Y.
42	Divinylbenzene	Dow Chemical Co., Midland, Mich.
		Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.
43	α-Hydroxy Isobutyrate Esters	American Cyanamid & Chemicals Corp., 30 Rockefeller Plaza, New York, N. Y.
44	Methacrylate Esters	Rohm & Haas Co., 222 W. Washington Square, Philadelphia, Pa.
		E. I. du Pont de Nemours & Co., Inc., Ammonia Dept., Wilmington, Del.
45	Acrylic Esters	Rohm & Haas Co., 222 W. Washington Square, Philadelphia, Pa.
	Polyhydricalcohol Methacrylates	E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
46	Methacrylic Anhydride	E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
47	Styrene	Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.
		Dow Chemical Co., Midland, Mich.
	Pentachlorodiphenyl	Hooker Electrochemical Co., 1942 Union St., Niagara Falls, N. Y.
		Dow Chemical Co., Midland, Mich.
		Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.
48	Quinoline	The Barrett Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.

Experiment	*Material*	*Sources*
50	Vinyl Acetate	Niacet Chemical Corp., 4702 Pine Ave., Niagara Falls, N. Y.
51	Polyvinyl Acetate	Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y. E. I. du Pont de Nemours & Co., Inc., Electrochemicals Division, Wilmington, Del. Niacet Chemical Corp., 4702 Pine Ave., Niagara Falls, N. Y.
53	Butyraldehyde	Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y.
	Dibutyl Sebacate	Griffin Chemical Co., 1000 Sixteenth St., San Francisco, Calif. Resinous Products & Chemicals Co., 222 W. Washington Square, Philadelphia, Pa.
	Diethylene Glycol Dihexoate	Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y.
57	Polyvinyl Chloride	Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y. The B. F. Goodrich Co., 1300 Rubber St., Akron, Ohio.
	Polyvinyl Chloride Copolymers	Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y.
	Rubber Mill	Wm. R. Thropp & Sons Co., 968 E. State St., Trenton, N. J. L. Albert & Sons Co., 300 Whitehead Rd., Trenton, N. J. Farrell-Birmingham Co., 475 N. Cliff St., Ansonia, Conn.
61	Diallyl Phthalate	Shell Chemical Co., San Francisco, Calif.
	Allyl Alcohol	R. W. Greeff & Co., Inc., 10 Rockefeller Plaza, New York, N. Y.
62	Butenyl Alcohols	Shell Chemical Co., San Francisco, Calif.
	Allyl Ethyl Ether	From Allyl Chloride and Sodium Ethylate.
	Diallyl Ether	Shell Chemical Co., San Francisco, Calif.
	Dimethallyl Ether	Shell Chemical Co., San Francisco, Calif.
64	Dimethyl Maleate	National Aniline Division, Buffalo, N. Y.
66	Chloromaleic Anhydride	National Aniline Division, Buffalo, N. Y.
69	Acrylonitrile	Rohm & Haas Co., 222 W. Washington Square, Philadelphia, Pa. American Cyanamid & Chemicals Corp., Rockefeller Plaza, New York, N. Y.
70	Copolymer of Vinyl Chloride and Vinyl Acetate—the Vinylite Series	Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y.
71	Methacrylonitrile	Resinous Products & Chemicals Co., 222 W. Washington Square, Philadelphia, Pa.
73	Butadiene	Ohio Chemical & Manufacturing Co., 1176 Marquette St., N.E., Cleveland, Ohio.
	Dodecyl Mercaptan	Hooker Electrochemical Co., Buffalo, N. Y.
	N-Phenyl-β-Naphthylamine	Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.
74	Carbon Black	Columbian Carbon Co., 45 E. 42nd St., New York, N. Y. Godfrey L. Cabot, 77 Franklin St., Boston, Mass.
	Mercaptobenzothiazole	R. T. Vanderbilt & Co., 230 Park Ave., New York, N. Y. Naugatuck Chemical Co., Naugatuck, Conn.
76	Sodium Tetrasulfide	Hooker Electrochemical Co., Buffalo, N. Y.
79	Primary Cellulose Acetate	Hercules Powder Co., Inc., Wilmington, Del. Tennessee-Eastman Corp., Kingsport, Tenn.
	Secondary Cellulose Acetate	Hercules Powder Co., Inc., Wilmington, Del. Tennessee-Eastman Corp., Kingsport, Tenn.
	Cellulose Nitrate	E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. Nixon Nitration Works, Nixon, N. J. Monsanto Chemical Co., Plastics Division, Springfield, Mass.
	Cellulose Acetate Butyrate	Tennessee-Eastman Corp., Kingsport, Tenn.
	Methylcellulose	Rohm & Haas Co., 222 W. Washington Square, Philadelphia, Pa.
	Ethylcellulose	Dow Chemical Co., Midland, Mich. Hercules Powder Co., Inc., Wilmington, Del.
	Hydroxyethylcellulose	Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y.
	Sodium Carboxymethylcellulose	Hercules Powder Co., Inc., Wilmington, Del.
80	Dimethyl Phthalate	Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.

Experiment	*Material*	*Sources*
	Diethyl Phthalate	The Barrett Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.
		U. S. Industrial Chemicals, Inc., 60 E. 42nd St., New York, N. Y.
	Fractol A	Standard Oil Company of Indiana, 910 S. Michigan Ave., Chicago, Ill.
	Poly-pale Ester Gum	Hercules Powder Co., Inc., Wilmington, Del.
	Japan Wax	American Cyanamid & Chemicals Corp., 30 Rockefeller Plaza, New York, N. Y.
81	Coumarone Resin	Barrett Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.
	Age Rite Alba Stabilizer	R. T. Vanderbilt & Co., 230 Park Ave., New York, N. Y.
84	Hexamethylenediamine	May or may not be obtainable from du Pont but can be synthesized from hexamethylene dibromide, using Gabriel's synthesis, or by degrading Nylon with concentrated HCl.
86	Casein	American Cyanamid & Chemicals Corp., 30 Rockfeller Plaza, New York, N. Y.
		Casein Corporation of America, Division of Borden Co., 350 Madison Ave., New York, N. Y.
87	Benzenedisulfonamide	From ammonia and any of the pure benzene disulfonic acids of their mixtures through the acid chlorides.
	Benzenedisulfonic Acids	Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.
	Benzene- or Toluenesulfonamide	Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.
88	Aniline	National Aniline Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.
		E. I. du Pont de Nemours & Co., Inc., Explosives Dept., Wilmington, Del.
		Calco Chemical Division, American Cyanamid & Chemical Corp., Bound Brook, N. J.
	Sulfanilamide	Calco Chemical Division, American Cyanamid & Chemical Corp., Bound Brook, N. J.
		Monsanto Chemical Co., 1700 S. Second St., St. Louis, Mo.
	Aminophenols	E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
89	Furfuryl Alcohol	Quaker Oats Co., 141 W. Jackson Blvd., Chicago, Ill.
90	Indene	The Barrett Division, Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.
		Reilley Tar & Chemical Corp., Merchants Bank Bldg., Indianapolis, Ind.
91	Rosin	Hercules Powder Co., Delaware Trust Bldg., Wilmington, Del.
	Shellac	Adolphe Hurst & Co., Inc., 328 W. 42nd St., New York, N. Y.
		W. Zinsser & Co., Inc., 516 W. 59th St., New York, N. Y.
95	Ammonium Sulfamate	E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
96	Phenylenediamine	E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
		Eastman Kodak Co., Rochester, New York.
97	Quebraco Tannin or Extract	American Cyanamid & Chemicals Corp., 30 Rockefeller Plaza, New York, N. Y.
Test Method		
3	Milk Dishes	No. 8-732—Aluminum Weighing Dishes, Eimer & Amend, 633 Greenwood St., New York, N. Y.
4	Stroke Cure Electric Plate	Thermo-Electric Co., 1012 West Superior Avenue, Cleveland 13, Ohio.
7	Ostwald Viscometer Apparatus	Precision Scientific Co., 1730 N. Springfield Ave., Chicago, Ill.