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Preparation of Thermosetting Hydrocarbon Resin

Resins from Formaldehyde, LXIII¹⁾.

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(Eingegangen am 8. November 1960)

SUMMARY:

A study to obtain a resin consisting only of carbon and hydrogen and yet having thermosetting properties was made. The process was a reaction of xylene-formaldehyde resin (XF-resin) with a hydrocarbon (CH):



The reaction was assumed to proceed through an electrophilic substitution. To find some reactive hydrocarbons, 15 different aromatic hydrocarbons have been reacted with formaldehyde in the presence of perchloric acid. It was found that acenaphthene, acenaphthylene, anthracene and mesitylene easily reacted with formaldehyde. Some XFresins were prepared, and reacted with the mentioned aromatic hydrocarbons.

Of these hydrocarbons, acenaphthene, polyacenaphthylene and acenaphthene-formaldehyde resin were especially effective.

It is understandable that an ω, ω' -dimethylol-XF-resin is more effective than a normal XF-resin. So an useful method for the synthesis of the ω, ω' -dimethylol-XF-resin was investigated.

By the reaction of ω,ω' -dimethylol-XF-resin with accempthhene-formaldehyde resin in the presence of xylene sulfonic acid, the desired cured resin was obtained. The resin consisted only of carbon and hydrogen. It was insoluble in benzene and non-melting. (However, by changing the conditions, anthracene or mesitylene can also cure XF-resins).

¹⁾ The foregoing paper of this series: Part LII, M. IMOTO, C. Y. HUANG, J. HASHIZUME, S. SANO, and K. AMAMIYA, J. chem. Soc. Japan, ind. Chem. Sect. 63 (1960) 1807.

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ZUSAMMENFASSUNG:

Um ein "härtbares" Harz zu erhalten, das nur aus Kohlenstoff und Wasserstoff besteht, wurde ein Xylol-Formaldehyd-Harz (XF-Harz) mit einem Kohlenwasserstoff (CH) wie folgt umgesetzt:



Es wurde dabei angenommen, daß hierbei eine elektrophile Substitution erfolgt. Auf der Suche nach reaktionsfähigen Kohlenwasserstoffen wurden 15 verschiedene aromatische Verbindungen in Gegenwart von Perchlorsäure mit Formaldehyd umgesetzt. Dabei reagierten Acenaphthen, Polyacenaphthylen, Anthracen und Mesitylen leicht mit Formaldehyd. Es wurden nunmehr XF-Harze hergestellt und mit den erwähnten aromatischen Kohlenwasserstoffen umgesetzt. Dabei waren Acenaphthen, Polyacenaphthylen und Acenaphthen-Formaldehydharz besonders wirksam.

Da ein ω, ω' -Dimethylol-XF-Harz bei der Umsetzung noch wirksamer als ein normales Harz sein sollte, wurde eine brauchbare Methode für die Herstellung eines ω, ω' -Dimethylol-XF-Harzes entwickelt. Durch Umsetzung des ω, ω' -Dimethylol-XF-Harzes mit Acenaphthen-Formaldehyd-Harz in Gegenwart von Xylolsulfonsäure wurde schließlich ein gezielt vernetztes Harz erhalten, das nur aus Kohlenstoff und Wasserstoff bestand. Es ist unschmelzbar und in Benzol unlöslich.

(Unter geänderten Bedingungen kann auch Anthracen oder Mesitylen das XF-Harz vernetzen).

Introduction

We have prepared a *m*-xylene-formaldehyde resin (XF-resin) and have carried out a series of researches to cure the resin with phenol, phenolformaldehyde resin, aniline or their derivatives²). A part of these studies has already been industrialized.

The reaction scheme is summarized in the following Figure 1.

As can be seen from the above figure, half of the cured resin consists of phenol nuclei. Therefore, the electric insulation and the resistance to alkali of the resulting resin are considerably improved compared with the phenol-formaldehyde resin. For instance, in the case of laminate from

R. WEGLER, Angew. Chem. 60 (1948) 88; C. Y. HUANG, M. IMOTO et al., J. chem. Soc. Japan, ind. Chem. Sect. 58 (1955) 517, 520; 60 (1957) 1573, 1576, 1579, 1582; 62 (1959) 273, 276, 279.



Fig. 1. Scheme of the formation of a cured XF-phenol resin

paper and resin, the insulation property increases to 10^7 compared with 10^5 meg.-ohm cm. for the phenol-formaldehyde resin. Further, if it is possible to replace the whole phenol nuclei by hydrocarbons, the electrical resistance will increase to almost as high as those of polystyrene or polyethylene. Moreover, as they are thermosetting resins, they have a good heat stability and also mechanical strength not inferior to the phenol-formaldehyde resin.

For such a purpose, we have made a study to obtain a resin consisting only of carbon and hydrogen and yet possessing thermosetting properties. As of date, we have almost accomplished this aim, though only on a laboratory scale. We shall now describe it briefly. The present paper is a summary of Parts LV, LVII, LVIII, LIX, LX, LXI, and LXII of "Resins from Formaldehyde" and its content is as follows:

- 1. Reactivity of aromatic hydrocarbons with formaldehyde³⁾.
- 2. Reaction of primary *m*-xylene-formaldehyde resin (XF-resin) with anthracene⁴).
- 3. Reaction of XF-resin with mesitylene⁵⁾.
- 4. Reaction of XF-resin with poly-acenaphthylene⁶⁾.
- ³⁾ Part LV: M. IMOTO, C. Y. HUANG, S. YOSHIOKA, and T. UEHARA, J. chem. Soc. Japan, ind. Chem. Sect., in press.
- ⁴⁾ Part LVIII: C. Y. HUANG, F. SAKURAI, and M. IMOTO, J. chem. Soc. Japan, ind. Chem. Sect., in press.
- ⁵⁾ Part LIX: M. IMOTO, C. Y. HUANG, and F. SAKURAI, J. chem. Soc. Japan, ind. Chem. Sect., in press.
- ⁶⁾ Part LVII: M. IMOTO, C. Y. HUANG, and T. IGUCHI, J. chem. Soc. Japan, ind. Chem. Sect., in press.

- 5. Reaction of primary naphthalene-formaldehyde resin or XF-resin with acenaphthene⁷⁾.
- 6. Synthesis of poly-(4,6-dimethyl)-xylylene glycol⁸⁾.
- 7. Curing of poly-(4,6-dimethyl)-xylylene glycol with acenaphtheneformaldehyde resin⁹⁾.

Adding to these, a study on the reaction of polyvinyl-*m*-xylene with formaldehyde was made as Part LVI of this series and has already been printed¹⁰.

1. Reactivity of Aromatic Hydrocarbons with Formaldehyde³⁾

Our principle to prepare thermosetting hydrocarbon resin lies in that we intend to use some reactive hydrocarbon to replace the phenol as indicated in Fig. 1. The curing reaction takes place in the presence of an acid. The reaction is an electrophilic substitution, as shown below:



Accordingly, it is of first importance to find such a hydrocarbon, suitable for an electrophilic reaction. It should be an aromatic hydrocarbon. Therefore, the reactions between 15 kinds of aromatic hydrocarbons and formaldehyde were tested in the presence of perchloric acid. In these cases, formaldehyde undergoes reaction as a methylol cation.

$$CH_2O_{aq.} + H^+ \longrightarrow +CH_2OH$$

⁷⁾ Part LX: M. IMOTO, C. Y. HUANG, and T. KURAYA, J. chem. Soc. Japan ind. Chem. Sect., in press.

⁸⁾ Part LXI: M. IMOTO, C. Y. HUANG, and J. ITAKURA, J. chem. Soc. Japan, ind. Chem. Sect., in press.

⁹⁾ Part LXII: M. Imoto and C. Y. HUANG, J. chem. Soc. Japan, ind. Chem. Sect., in press.

¹⁰) Part LVI: T. IGUCHI, C. Y. HUANG, and M. IMOTO, Makromolekulare Chem. 40 (1960) 200.

Consequently, it is considered that hydrocarbons having high reactivity with formaldehyde in an acidic medium are suitable for an electrophilic reaction with primary XF-resin.

1.1 Experimental

Purified acetic acid was used as solvent. Paraformaldehyde (abbreviated as F hereafter) was dissolved into acetic acid to give a solution of 0.03-0.17 mole/l. The concentration od the hydrocarbon (abbreviated as RH) in the reaction system was the same as that of F (0.03-0.17 mole/l.).

Perchloric acid (abbreviated as C) was used as 0.12% solution in acetic acid and the concentration in the reaction mixture was kept at $3 \cdot 10^{-2}$ mole/l. The rate of the reaction was measured by titrating the existing quantity of F. The quantitative analysis of F was made according to the KCN-Hg(NO₃)₂ method, using diphenylcarbazone as an indicator. The rate of reaction was calculated with the following equation:

$$-[F]/dt = k[F][RH]$$

Therefore, k obtained includes a constant value of [C].

1.2 Results

Results obtained are shown in Table 1. From the table, it was found that both acenaphthene and acenaphthylene have half the reactivity of *p*-cresol. *p*-Cresol reacts readily with formaldehyde, as is well-known.

RH	80 °C.	70 °C.	60 °C.	E(kcal./mol)
<i>p</i> -Xylene	0.672	0.293	0.126	20.2
m-Xylene	3.98	1.54	0.564	22.7
p-Xylene	0.197	0.077	0.029	23.6
<i>p</i> -Cymene	0.083	0.035		21.0
Mesitylene	223	98.3	40.1	20.8
1,2,4-Trimethylbenzene	13.00	6.10	2.77	20.0
Durene	2.99	0.850	0.233	(30.0)
Pentamethylbenzene	24.30	10.21	4.45	20.0
Naphthalene	0.465	0.168	0.059	24.8
α-Methyl-naphthalene .	6.13	2.18	0.735	24.9
β-Methyl-naphthalene .	4.76	1.63	0.553	24.8
Acenaphthene	1240	512.0	197.2	21.6
Acenaphthylene	2140	967.0	403.2	20.2
2,2',4,4'-Tetramethyl-				
diphenylmethane	38.70	14.28	5.48	23.0
p-Cresol	5130	2223	930	21.2

Table 1. Values of K (l/mole · sec.) and activation energy

Further, activation energy, E, was estimated as approximately 23 kcal./mol. IMOTO¹¹⁾ has long been stating that E of the reaction of formaldehyde is always about 23 kcal./mole in the presence of an acidic catalyst. Therefore, this was substantiated in this case, too.

Acenaphthene and mesitylene are small in value. It was also found that anthracene showed a considerable reactivity. It is, however, omitted from the list (Table I), owing to the fact that it produces a precipitate halfway during the reaction and does not become homogeneous. Due to the above reason, it was attempted in the following experiments to cure the primary XF-resin by the use of anthracene, mesitylene, acenaphthylene or acenaphthene.

2. Reaction of XF-Resin with Anthracene⁴)

In order to cure the primary XF-resin according to the process shown in Fig. 1, anthracene was used to replace phenol.

2.1 Preparation of primary XF-resin

A mixture of 530 g. of *m*-xylene, 860 g. of 37% formalin and 250 g. of concentrated H_2SO_4 was heated at 95 °C. for 5 hrs. Then, to this mixture was added 5 l. of benzene and the upper organic layer was separated, washed with water, dilute alkali solution and then dried with CaCl₂. After the benzene was distilled off, the unreacted *m*-xylene was recovered under 10 mm Hg to leave 530 g. of a light yellowish oily product. The molecular weight of the resin thus obtained was 310 and its oxygen content was 12.47%.

Changing the conditions, two other kinds of XF-resins were prepared. They are listed in Table 2.

No.	Mol.wt.	Oxygen-content $^{0}/_{0}$		
1	230	15.59		
2	310	12.47		
3	360	9.21		

Table 2. Primary XF-resins

2.2 Reaction of XF-resin with anthracene

To a mixture of 9.6 g. of resin No. 2 (see Table 2) and 5.5 g. of anthracene, 0.076 g. of *m*-xylene sulfonic acid was added and then heated. Fig. 2 indicates the increase of the molecular weight with the reaction time. The molecular weight was measured by the cryoscopic method in benzene. The oxygen-content was calculated by the elementary analysis:

$$O^0/_0 = 100 - (C^0/_0 + H^0/_0).$$

¹¹⁾ M. IMOTO and H. KAKIUCHI, Chem. High Polymers Japan 5 (1948) 117.









Fig. 3. Mol.wt. of the reaction products of XF-resin with anthracene vs. the amount of the catalyst

¹²⁾ Changing the reaction conditions, it was found that a cured product was obtained by the reaction of XF-resin with anthracene or mesitylene. These results shall be published later.

The molecular weight of the product increased with the amount of the catalyst used as shown in Fig. 3. The conditions of the reaction were as follows: primary XF-resin No. 2 9.6 g., anthracene 5.5 g., *m*-xylene sulfonic acid 0.076 0.19 g., reaction temp. 140 °C.

The oxygen-content in the primary XF-resin indicated a remarkable effect on the molecular weights of the reaction products, as illustrated in Fig. 4. The conditions for the reaction were as follows: XF-resin 9.6 g., anthracene 5.5 g., *m*-xylene sulfonic acid 0.076 g., 140 °C.



Fig. 4. Increase in mol.wt. of the reaction products from various XF-resins with anthracene vs. the time of reaction

 \circ = XF-resin, No. 1, O = 15.59% \triangle = XF-resin, No. 2, O = 12.47% • = XF-resin, No. 3, O = 9.21%

The higher the oxygen-content in the primary resin, the larger is the increase in molecular weight of the reaction product. Fig. 5 shows the rate of the decrease of oxygen-content by the reaction mentioned in Fig. 4.

2.3 Determination of the reacted positions of anthracene

In order to determine the position in which the anthracene reacted with the XF-resin, anthracene was treated with 2,4-dimethyl benzyl alcohol according to the following scheme:



Fig. 5. Decrease of the oxygen-content of the reaction product vs. time

9,10-Bis-(2,4-dimethyl-benzyl)-anthracene (I). 13.6 g. of 2,4-dimethyl benzyl alcohol and 4,65 g. of anthracene were heated for 6 hrs. at 165 °C. in the presence of 0.18 g. of *m*-xylene sulfonic acid. The reaction mixture was recrystallized four times from benzene to give 6.8 g. of I. M.p. 275–276 °C.

Anthraquinone (II). 0.3 g. of I was oxidized with 1.5 g. of CrO_3 in 100 ml. of acetic acid. Anthraquinone obtained showed a m.p. of 286 °C. and no m.p. depression was obtained with an original specimen.

From these reaction, it was assumed that the reaction of the primary XF-resin with anthracene proceeded via following scheme:



3. Reaction of Primary XF-Resin and Mesitylene⁵⁾

In order to cure the XF-resin according to the process shown in Fig. 1, mesitylene was used to replace phenol. Mesitylene, as was shown in Table 1, possesses a reactivity of 0.04 times that of p-cresol and is a three functional compound at the same time.

3.1 Reaction of XF-resin with mesitylene

A mixture of 15.5 g. of No. 2 resin (cf. Table 2), 6.0 g. of mesitylene and 0.215 g. (1% of the total amount) of *m*-xylene sulfonic acid was heated





at a constant temperature. Fig. 6 shows the increase in the molecular weight according to the reaction time. With higher temperatures, the molecular weight increases more quickly.

The oxygen-content of the reaction product decreased with the reaction time, as shown in Fig. 7.



Fig. 7. Variation of the oxygen-content depending on the reaction time

The effect of the amount of *m*-xylene sulfonic acid as catalyst on the increase in mol.wt. of the reaction product is illustrated in Fig. 8. The conditions for the reaction were as follows: XF-resin No. 2, 15.5 g., mesitylene 6.0 g., *m*-xylene sulfonic acid 0.108-0.260 g., reaction temp. 150 °C.



Fig. 8. Effect of the amount of the catalyst on the mol.wt. of the reaction product -

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As in the case of anthracene, the higher the oxygen-content of the XFresin, the mol.wt. of the reaction product increases more rapidly. This result is shown in Fig. 9, using three kinds of XF-resins.



Fig. 9. Effect of the oxygen-content of XF-resin on the increase in mol.wt. of the reaction product. Amount of catalyst 1%; Reaction temp. 150 °C.

From the above-mentioned facts, it was concluded that XF-resins reacted with mesitylene to increase the molecular weight of the product, but no insoluble matter in benzene was obtained¹²). Accordingly, mesitylene performed as a bifunctional compound, contrary to our expectations, at the temperature below 160 °C.

3.2 Process of the reaction of the XF-resin with mesitylene

From the evidence of the following two reactions it is shown that the reaction of the XF-resin with mesitylene is according to the scheme in Fig. 1.



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(a) Reaction of 2,4-dimethyl benzyl alcohol with mesitylene. A mixture of 2,4-dimethyl benzyl alcohol 13.6 g., mesitylene 60 g. and *m*-xylene sulfonic acid 0.73 g. was heated. 2,4,2',4',6'-Pentamethyl diphenyl methane (III) was obtained as a colorless oil. B.p. 170 to $172 \,^{\circ}$ C. (5 mm Hg).

(b) Reaction of bis-(2,4-dimethyl benzyl)-ether with mesitylene. A mixture of bis-(2,4-dimethyl benzyl)-ether 6.4 g., mesitylene 30 g. and *m*-xylene sulfonic acid 6.36 g.was heated for 6 hrs. and a product same as that in (a) was obtained. B.p. 148-150 °C. (3 mm Hg).

Anal.: Found C 91.00 H 9.07 Mol.wt. found 240

3.3 Comparison of the reactivity between mesitylene and anthracene

1% of *m*-xylene sulfonic acid was added to a mixture of XF-resin No. 2 and mesitylene or anthracene and heated at 150 °C. The rate of increase of mol.wt. of the reaction product is shown in Fig. 10. It was concluded that anthracene was more reactive than mesitylene.



Fig. 10. Comparison of the reactivity between mesitylene and anthracene

4. Reaction of XF-Resin with Polyacenaphthylene⁶)

In order to cure the primary XF-resin according to the process shown in Fig. 1, polyacenaphthylene was used to replace phenol. The polymerization of acenaphthylene has been described, using $BF_3 \cdot Et_2O^{13}$ or the ZIEGLER-type catalyst $(Ti(OBu)_4$ -LiAlH₄ or $Ti(OBu)_4$ -AlEt₃)¹⁴⁾.

Polyacenaphthylene (IV) used in this experiment was obtained through radical polymerization using benzoyl peroxide as initiator. As described above, acenaphthylene reacts easily with formaldehyde in the presence of acid. Accordingly, it can be anticipated that the primary XF-resin undergoes a cross-linking reaction with polyacenaphthylene through a cationoid substitution reaction. The process may be shown as in the following scheme:



4.1 Material

Primary XF-resins have the following properties.

Table 3. Properties of XF-resins

	XF-1	XF-2	XF-3	• XF-p*)
	280	296	408	770
Oxygen-content (%)	12.77	8.09	8.06	11.18

*) XF-p was poly-(4,6-dimethyl)-xylylene glycol which was obtained by polycondensation of m-xylenedimethylol compound.

Polyacenaphthylene was prepared by polymerization as shown in the following table:

- 13) M. IMOTO and K. TAKEMOTO, J. Polymer Sci. 15 (1955) 271.
- ¹⁴⁾ M. IMOTO and I. SOEMATSU, Bull. chem. Soc. Japan 34 (1961) 26.

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	PA-1	PA-2
Acenaphthylene (g.)	100	120
Bz_2O_2 (g.)	5	0.60
Toluene (g.)	250	0
Reaction temp. (°C.)	98-99	98-99
Reaction time (hrs.)	6	7
Yield (%)	87	79
Softening pt. (°C.)	270-290	310-325
[η] (25 °C., Benzene)	0.0502	0.2252

Table 4. Preparation and properties of polyacenaphthylene

4.2 Experimental and results

 $(0.5-1.0) \cdot 10^{-2}$ mole of the primary XF-resin was mixed with an molar equivalent amount of polyacenaphthylene and 0.5-1.0 % of *m*-xylene sulfonic acid. The mixture was then heated at the required temperature. The working up treatment was in accordance with the following scheme:

The product was grounded into pieces \downarrow Washing with 1% NaOH aq. to separate X-SO₃H

Benzene extraction



Fig. 11. Scheme for the working up-treatment

The results obtained are shown in Fig. 12, when a mixture of $1.0 \cdot 10^{-2}$ mole of XF-resin and 1.5 g. of PA-1 was heated at 150 ± 1 °C. with *m*-xylene sulfonic acid in an amount of 1 % based on the XF-resin.

By heating the XF-resin only, its mol.wt. increased, as shown in Fig. 12. However, the increase was very small, compared with that in the case with acenaphthylene or polyacenaphthylene, and gelation did not occur.



Fig. 12. Mol.wt. of the soluble part (XF-Fraction) and amount of insoluble part vs. time $\circ = XF-1$ and PA-1 $\Box = XF-2$ and PA-1 $\triangle = XF-3$ and PA-3

In the experiments illustrated in Fig. 12, intrinsic viscosity and oxygencontent of PA-fraction were measured. The results are shown in Fig. 13.



Fig. 13. $[\eta]^{25^\circ}_{\text{Benzene}}$ and oxygen-contents of PA-fractions vs. time of reaction

 $\circ = XF-1 \text{ and } PA-1$ $\Box = XF-2 \text{ and } PA-1$ $\Delta = XF-3 \text{ and } PA-1$



Fig. 14. Effect of amount of *m*-xylene sulfonic acid on gelation (measured from the weight of insoluble part in benzene) and $[\eta]$ of PA-fraction

 $\bigcirc = XSO_{3}H \ 1.0 \ \%$ $\square = XSO_{3}H \ 0.75 \%$ $\triangle = XSO_{3}H \ 0.50 \%$

Fig. 14 indicates the effects of amount of the catalyst on the curing of XF-resin (measured by the amount of the insoluble fraction in benzene) and the intrinsic viscosity of PA-fraction. The conditions for this experiment were as follows: 2.80 g. of XF-1, 1.50 g. of PA-2, varied amount of X-SO₃H; reaction temperature, 150 °C.

The effects of reaction temperature are shown in Fig. 15, where a mixture of 2.80 g. of XF-1, 1.50 g. of PA-2 and $1^{0}/_{0}$ of X-SO₃H.



Fig. 15. Effects of reaction temperature on gelation and $[\eta]$ of PA-fraction

$$\circ$$
 = Reaction temp. 150 ± 1 °C.

 \Box = Reaction temp. 140 ± 1 °C.

 \triangle = Reaction temp. 130 ± 1 °C.

From the results, it was concluded that XF-1, the resin of low mole cular weight and high oxygen-content, was most easily gelatinised.

4.3 Process of the reaction of XF-resin with acenaphthylene

In order to testify that the curing reaction was carried out according to the scheme shown in Fig. 1, a synthesis of 2,4-dimethyl-benzylacenaphthylene (V) was carried out.



(1) A mixture of 3.4 g. (0.025 mole) of 2,4-dimethyl benzyl alcohol and 31 g. (0.20 mole) of acenaphthylene was heated at 140–145 °C. for 1.5 hrs. in the presence of 0.2 g. of *m*-xylene sulfonic acid. 1.75 g. of white crystals were obtained. M.p. 82–83 °C. (recrystal-lized from methanol).

Anal.: C₂₁H₂₀ Calc. C 92.60 H 7.40 Mol.wt. 272.4 Found C 92.38 H 7.60 Mol.wt. 268

(2) From bis-(2,4-dimethyl)-benzyl ether. 6.5 g. of bis-(2,4-dimethyl)-benzyl ether and 31 g. of acenaphthylene were heated at 160-165 °C. for 1.5 hrs. in the presence of 0.2 g. of *m*-xylene sulfonic acid. 2.5 g. of pure 2,4-dimethyl benzyl acenaphthylene were obtained. M.p. 82-83 °C. Mixing with the sample described above, no depression in the melting point was observed,

> Anal.: C₂₁H₂₀ Calc. C 92.60 H 7.40 Mol.wt. 272.4 Found C 92.38 H 7.60 Mol.wt. 268

Reaction of XF-Resin and Naphthalene-Formaldehyde Resin with Acenaphthene or Acenaphthene-Formaldehyde Resin⁷)

Naphthalene reacts with formaldehyde in the presence of sulfuric acid in the same way as *m*-xylene to form naphthalene-formaldehyde resin¹⁵. This is called the primary NF-resin.



¹⁵⁾ C. Y. HUANG, T. KURAYA, and M. IMOTO, unpublished.

Primary NF-resin can also be cured by phenol or novolac resins. Here, XF-resin and NF-resin were reacted with acenaphthene and acenaphthene-formaldehyde resin (AF-resin)¹⁶) in order to be cured.

5.1 Material

Molecular weights and oxygen-contents of three kinds of primary resins used in these experiments are shown in Table 5. Besides AF-resin, acenaphthene and acenaphthylene were used as curing agents.

	XF-resin	• NF-resin	AF-resin ¹⁶⁾
Mol.wt	478	422	555
Oxygen-content (%) $\dots \dots$	9.61	7.54	1.93

Table 5. Properties of the resins

5.2 Reaction of XF-resin and NF-resin with acenaphthene

m-Xylene sulfonic acid was used as catalyst. The same procedure as in the above experiments for the curing was adopted. From the reaction mixture obtained, both catalyst and acenaphthene were removed completely by the extraction with methanol and the residue was then extracted with benzene at a raised temperature. Thus, the insoluble part was separated. The receipts for the reaction are shown in Table 6.

Table 6. Receipts for the curing experiments

	Primary resin	Acenaphthene	Xylene SO ₃ H
XF resin	6 g.	2 g.	0.08 g. (1%)
NF resin	5 g.	3.5 g.	0.2 g. (2.35%)

While the duration of the reaction was kept constant at 60 min., the reaction temperature was varied from $150 \,^{\circ}$ C. to $210 \,^{\circ}$ C. The results obtained are illustrated in Fig. 16. Percentages of gelation indicated the weight % of the insoluble part formed in relation to the primary resin.

It attracted attention that the NF-resin did not cure or was very difficult to cure. To confirm this behavior of the NF-resin, the effects of reaction time were tested and these results are shown in Fig. 17. The conditions were the same as those in the former case. It was also found that NF-resin produced no insoluble part.

¹⁶⁾ T. TANIGAKI, unpublished.









Fig. 17. Effects of reaction time on the curing reaction

Effects of the amount of catalyst on the curing reaction are shown in Fig. 18.

Formerly, it was well established kinetically¹⁷ that the mol.wt. of the soluble part of resin decreased with the progress of gelation.

¹⁷⁾ M. IMOTO, M. OIWA, et al., Chem. High Polymers Japan 4 (1947) 102; 6 (1949) 244.



Fig. 18. Amount of catalyst in % based on the amounts of XF-resin and acenaphthene vs. yield of gelation and mol.wt. of the soluble fraction. XF-resin 6 g. Acenaphthene 2 g. 170 °C. 60 min.

Comparisons of the curing reactivities of acenaphthene and acenaphthylene were made as shown in Fig. 19. The amount of catalyst was 1 %, the reaction temperature 170 °C. and time 60 min.

5.3 Reaction of XF-resin with AF-resin



Fig. 19. Molar ratio of XF-resin to accenaphthene or poly-accenaphthylene vs. mol.wt. and % of gelation

(XF-resin, Catalyst $1.0^{0}/_{0}$; 170° C.; 60 min.) (NF-resin, Catalyst $2.4^{0}/_{0}$; 150° C.; 60 min.) Reactivity of AF-resin as curing reagent for XF-resin was studied. The results obtained are shown in Fig. 20. *m*-Xylene sulfonic acid was used in an amount of 1 % based on the total amount of resin.

The conclusions are as follows: (1) XF-resin was cured readily. The yield of gelation was better, when 3-3.5 g. of acenaphthene was added to 1 g. of XF-resin. When XF-resin was reacted with acenaphthene using a



yield of gelation and oxygen-content

catalyst, 3 % in quantity, at $170 \,^{\circ}$ C. for 60 minutes, 95 % of it was gelatinised. When gelation commenced, the molecular weight of the soluble part began to decrease. (2) The comparison in gelation of the XF-resin was in the following order.

AF-resin > acenaphtene > acenaphthylene

6. Synthesis of Poly-(4,6-dimethyl)-xylylene Glycol

From the above-mentioned facts, it was made clear that XF-resin (VI) can be cured to yield three dimensional macromolecules by reacting with polyacenaphthylene, acenaphthene or acenaphthene-formaldehyde resins.



But the xylene nucleus at both ends of the resin VI is monofunctional, so the curing reaction terminates at this point. If the two xylene nuclei at both ends have also reactive groups, the curing reaction becomes easier. For this purpose, poly-(4,6-dimethyl)-xylylene glycol (VII) was synthesized.



The process of the synthesis is in accordance with the following equation:



6.1 Polycondensation of 4,6-dimethyl-m-xylylene glycol

In a three-necked flask, equipped with a condensation water separation apparatus, a thermometer and a nitrogen inlet tube, 100 g. of 4,6-dimethylol-*m*-xylene and 0.5 g. of sulfamic acid were placed. The mixture was then heated in a thermostat kept at ± 2 °C. The contents became viscous gradually, until at last it turned into a clear resin. Benzene wa then added to it and after washing completely with water, it was dried over Na₂SO₄. Then, the benzene was distilled off yielding a pale yellow resin. The softening point of the resulted resin was 85–95 °C. As it is a polyether-type XF-resin, it was called PEXF-resin.

The results of the kinetic studies can be seen in Fig. 21-23. Fig. 21 indicates the results obtained in the experiments carried out at 200 °C. The effect of reaction temperature on molecular weight of the polyether produced is seen in Fig. 22.

Oxygen-content of poly-(4,6-dimethyl)-m-xylylene glycol (abbreviated as PEXF-resin) decreased with increasing mol.wt., as shown in Fig. 23.

In general, both the theoretical and the experimental value of the oxygen-content coincided well, as long as the molecular weights were small. But, it seems that the larger the molecular weight, the smaller



Fig. 21. Mol.wt. of poly-(4 6-dimethyl)-m-xylene glycol vs. time of reaction

became the experimental value compared with the theoretical. For instance, when the molecular weight was 2,200, the theoretical value was 11.4 %, while the experimental one remained 11.1 %. But partly because the measured molecular weight was likely to become a rather too large,



Fig. 22. Mol.wt. of poly-(4,6-dimethyl)-m-xylene glycol vs. reaction temperature. Reaction time 50 min.

Dimethylol-m-xylene 100 g., Sulfamic acid 0.5 g.

owing to the adoption of freezing point depression method in benzene, and, partly, because oxygen content was calculated as [100-(C+H)] % an error of 0.3 % might come in question.



Fig. 23. Mol.wt. of PEXF-resin vs. its oxygen-content

Therefore, the fact that the actually measured value of oxygen-content is smaller than the theoretical could not be regarded as deformalization $(-CH_2OCH_2- \rightarrow -CH_2-+CH_2O)$. Even if this reaction took place, the yield may be very small and almost negligible.

6.2 Synthesis of 4,6-dichloromethyl-m-xylene

This depends on the following scheme:



4,6-dichloromethyl-m-xylene was synthesized from the reaction of m-xylene with formaldehyde in the presence of hydrochloric acid. The results are tabulated in Table 7.

3-Chloromethyl-*m*-xylene was a pale yellow oil, boiling at 95—96 °C./10 mm Hg. Anal.: C₉H₁₁Cl Calc. C 70.08 H 7.19 Found C 69.88 H 7.37

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4,6-Chloromethyl-m-xylene, colorless crystals, melting at 96–98 °C. and boiling at 146 to 148 °C./10 mm Hg.

Anal.: C₁₀H₁₂Cl₂ Calc. C 59.13 H 5.96 Found C 59.02 H 6.01

No.	m vylana	Formalin	n Formalin	HCl	HCI	Product	
of	mol.	mol.	mol.	conc.	gas	Mono-CH ₂ Cl	Di-CH ₂ Cl
Exp.				mol.	mol.	g.	g
1	1	2		10	—	82	79
3	1	4	_	10	-	60	106
8	1		3	10	_	56	107
11	1	3		10	3	46	131
12	1		5	10	4	10	170

Table 7. Chloromethylation of m-xylene

6.3 Synthesis of poly-(4,6-dimethyl)-m-xylylene glycol from 4,6-chloromethyl-m-xylene

Polyetheration of 4,6-dichloromethyl-*m*-xylene was accomplished through the reaction of it with NaOH in an autoclave. In an autoclave (content, 350 ml.), were added 4,6-chloromethyl-*m*-xylene 20.30 g. (0.1 mol.), NaOH, water 190 g. and benzene 152 ml. The mixture was then heated to the required temperature with stirring.



Fig. 24 shows the effects of the amount of NaOH. Abscissa was the molar ratio of 2 NaOH to dichloromethyl xylene. Mol.wt. of PEXF-resin obtained were determined cryoscopically, using benzene or camphor as

solvent (Oxygen-content was found from elementary analysis of C and H, according to the relation of O % = 100 - (C + H) %). The found values were compared with those calculated from mol.wt., assuming the products had the structure of ω,ω' -dimethylol polyether (VII).

When the molar ratio of 2 NaOH exceeded over 1.0, molecular weights of the products decreased steeply. Since the molecular weight of $HOCH_2-C_6H_2(CH_3)_2-CH_2OH$ is 166, it was concluded, no polyether was produced.



Fig. 26. Effect of time of reaction 150 °C. Molar ratio of 2NaOH/C₁₀H₁₂Cl₂, 0.923

Kept the molar ratio of 2 NaOH to dichloromethyl-xylene constant at 0.923, the temperature and reaction time were varied to obtain Fig. 25 and 26.

Thus, we could accomplish our goal by the use of NaOH, a little less in quantity than that needed for hydrolysis. The product contained no chlorine (determined by BEILSTEIN-test). As is shown in Fig. 24, if excess NaOH, more than equivalent, was used, the molecular weight of the formed polyether decreased greatly and the reaction tended to produce only dimethylol-*m*-xylene. That is, it was necessary to be acidic for the polyetheration. And if the quantity of NaOH was less than equivalent, the following reaction takes place.

$$-CH_2Cl + H_2O \rightarrow -CH_2OH + HCl$$

HCl thus formed helped polyetheration as follows;

$$-CH_2OH + H^+ \rightarrow -CH_2^+ + H_2O$$
$$-CH_2^+ + -CH_2OH \rightarrow -CH_2OCH_2^- + H^+$$

When dimethylol-*m*-xylene was heated at 200 °C. with 0.1 % of dichloromethyl-*m*-xylene, it also gave polyether. In this case, the HCl produced in the following reaction, was assumed to play a role of catalyst:

$$-CH_2Cl + -CH_2OH \rightarrow -CH_2OCH_2 - + HCl$$

7. Curing of PEXF-resin with Acenaphthene-Formaldehyde Resin



Fig. 27. Curing of PEXF-resin with AF-resin at 160 °C. Time of reaction 20 min.

O: Oxygen-content of the soluble part

 \times : Oxygen-content of the insoluble part

Material: AF-resin was obtained from acenaphthylene and 37% formalin in acetic acid. Mol.wt., 600; softening point, 77-84 °C.; C 92.60%; H 6.48%; oxygen-content, 0.92%. PEXF-resin was obtained as mentioned above. Mol. wt. 730; softening point, 55-62 °C.; oxygen-content, 12.03%; Cl, 0.00%.

Procedure: PEXF-resin 4.44 g., AF-resin 1.68 g., and *m*-xylene sulfonic acid (0.33 to 5.15% of the total quantity) were heated at 160 °C. or 190 °C. for 20 or 40 minutes. The insoluble part was separated with benzene. The results obtained are shown in Fig. 27 and 28.



Fig. 28. Curing of PEXF-resin with AF-resin at 190 °C. Time of reaction 40 min.



Fig. 29. Curing scheme of poly-(4,6-dimethyl)-xylylene glycol with acenaphthene-formaldehyde resin

Curing reaction proceeded easily. The reaction was assumed to proceed as shown in Fig. 29.

Effects of temperature and duration of the curing reaction are illustrated in Fig. 30 and 31.



Fig. 30. Effect of reaction temperature PEXF-resin 4.44 g.; AF-resin 1.68 g.; Catalyst 0.99 g.; 20 min.







Fig. 32. Effects of amount of AF-resin Temp. 160 °C. Time 20 min. Catalyst 0.09 g.

The effects of the molar ratio of the structural unit of AF-resin $(-CH_2-A-)$ to that of PEXF-resin $(-CH_2-X-CH_2-O-)$ are shown in Fig. 32. Curing took place only in the range of $\frac{0.006}{0.028} = \frac{0.02}{0.028}$ of the molar ratio. If AF-resin was added in more than the above-mentioned ratio, no curing occured.

The cured resin obtained, consisted of carbon and hydrogen. It was insoluble in benzene and non-melting. Its electrical and mechanical properties we will describe in later reports.