

Novel Epoxy Resins Based on Cyclohexanone-Aldehyde Condensation Products*

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Synopsis

Solid ketone-formaldehyde resins are used in certain coating formulations in order to improve hardness, gloss, and light stability. They are soluble, thermoplastic by nature, and contain limited amounts of hydroxyl groups. We found that their primary hydroxyls can be etherified with epichlorohydrin (ECH) either by a two-step ECH-addition/dehydrohalogenation procedure or by a one-step phase-transfer process. An intermediate of particular usefulness is the crystalline 2,2,6,6-tetramethyl-cyclohexanol (TMCH) made from cyclohexanone and 5 mol formaldehyde, yielding low colored epoxy resins with epoxy values up to 7.5 eq/kg. Depending upon the nature of the curing agent, high T_g solids as well as tough and flexible coatings with good outdoor stability can be made. Upon decreasing the formaldehyde-cyclohexanone ratio, solid condensation polymers melting up to 150°C can be obtained. Phase-transfer glycidylation yielded solid thermoset glycidyl ether resins with \bar{M}_n up to 1600, \bar{M}_w up to 13,000, epoxy values up to 3.6 eq/kg, and softening points between 80 and 160°C. Powder coatings formulated with carboxy-terminated polyesters are hard, glossy, solvent-resistant but somewhat brittle. In order to overcome this drawback, polycycloacetals have been produced from TMCH and glutardialdehyde, which are terminated by pairs of methylol groups. Powder coatings of the corresponding glycidylethers with carboxyl-terminated polyesters exhibited excellent flexibility and impact strength.

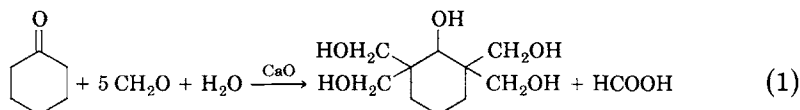
INTRODUCTION

Cyclohexanone resins have been known for a long time. They are generally prepared by base-catalyzed self-condensation of cyclohexanone and its derivatives or by cocondensation with aldehydes, preferably formaldehyde.¹⁻⁶ They are mainly solid resins, which are soluble in alcohols, esters, ketones, and aromatic hydrocarbons and useful in liquid coating formulations in combination with cellulose derivatives, alkyd resins, chlorinated rubber, and various copolymers based on vinyl esters, vinyl ethers, styrene, and acrylics, where they improve hardness,⁷ gloss, and light stability.⁸ Cyclohexanone-formaldehyde resins also have been modified with different reagents such as acetic anhydride, benzoyl chloride, hydroxylamine, semicarbazide, phenylhydrazine,⁹ and diisocyanates.¹⁰

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Little is known about the chemical structure of these resins. Carbonyl and hydroxyl groups, methylene and methylene ether bridges between the cyclohexanone (or -ol) nuclei seem to occur¹¹ in varying amounts depending on the molar ratio of ketone to formaldehyde, the alkali catalyst, and other condensation conditions. Except for the crosslinking of hydroxyl containing methyl-ethyl-ketone formaldehyde resins with isocyanates⁸ no thermoset polymers have been hitherto described on a ketone formaldehyde basis.

In our search for epoxy resins with improved UV and weather stability we became interested in cyclohexanone-formaldehyde condensation products with a high content of preferably primary hydroxyl groups. A well-defined compound can be made easily in a high yield according to the following equation¹²:



The etherification of the above 2,2', 6,6'-tetramethylol-cyclohexanol (TMCH) with epichlorohydrin can be carried out by two different processes, which have been developed previously in our laboratories.

1-Step Process. Reaction of TMCH with an excess of epichlorohydrin and with caustic soda under phase transfer conditions.

2-Step Process. Addition of an equivalent amount of epichlorohydrin in presence of a Lewis acid type catalyst and subsequent dehydrohalogenation with caustic soda. Both processes are described in more detail in the experimental part.

TMCH proved to be an excellent and well-defined ketone-formaldehyde model compound resulting in two epoxy resins with different molecular weight, viscosity, and chlorine content and with very desirable application properties as will be shown below. Further described is the preparation of glycidylethers of solid ketone-aldehyde resins, their properties and their application in coatings.

EXPERIMENTAL

Materials

Cyclohexanone was distilled once; aqueous formaldehyde solution (34 wt %) and epichlorohydrin were used as purchased from Fluka AG, Switzerland. Hexahydrophthalic anhydride, 4,4'-diaminodiphenylmethane, benzyl-dimethylamine, Araldite 6010, PT 810, the polyester resin Arakote 3003 and the hardener XU 283 are commercial products from Ciba-Geigy Corp. (Ardley, NY). The polyurethane coating was made from Glid-thane, a varnish from the Glidden Co. (Strongsville, OH).

Measurements

The hydroxyl and epoxy content were determined simultaneously according to the following Ciba-Geigy internal analytical method which comprises three

steps:

1. Acetylation of the OH groups with acetylbromide under liberation of 1 mol HBr per OH eq.
2. Opening of the oxirane ring by HBr.
3. Acetylation of the bromohydrin formed in step 2.

Excess of acetylbromide is hydrolyzed with pyridin/water, HBr, and acetic acid are titrated potentiometrically with 0.5N KOH in ethyl alcohol. Hydroxyl and epoxide content is calculated from the difference of both acids to those obtained from the hydrolyzed acetylating reagent. The carbonyl content was determined by titration with a solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$.¹³

A Waters liquid chromatograph was used for GPC measurements and for \bar{M}_n and \bar{M}_w determinations. The column (length 300 mm, diameter 7 mm) was packed with Ultrastyrigel, the resins were dissolved in tetrahydrofurane. IR spectra were recorded from resin coated KBr pellets by a Nicolet 20 2x FT-IR spectrophotometer.

Differential thermoanalyses were carried out on the TA-3000 analyzer from Mettler AG, Switzerland. The TMA-modulus 40 accessory to the above apparatus served for the determination of the glass transition temperature.

Room temperature viscosities were measured with the spindle viscosimeter from Brookfield Engineering Inc. (Stoughton, MA). At elevated temperatures a cone and plate viscosimeter from ICI was used. Softening points were determined on the Kofler heatbench from Reichert, Austria.

The mechanical properties of solids were determined on test bars cut from cast and cured plates (120 × 120 × 4 mm) according to the following "DIN test procedures": Flexural strength and elongation values were measured according to DIN 53452, impact strength according to DIN 53453, lap shear strength according to ISO 4587, heat distortion temperature according to DIN 53460, and the volume resistivity according to DIN 53482. The dielectric constant and the power factor were measured on a Schering bridge from Tettex AG, Zürich.

Powder coatings were made by melt mixing on a two-roll mill at 70°C during 6–7 min. Then they were ground on a pin-disc mill and sieved at 100 mesh. Coating properties were measured as follows: 60° gloss and yellowness index by BYK Chemie color and gloss meters. Reverse impact was performed on a Gardner Laboratory impact tester. Mandrel bend was performed on a conical mandrel by Gardner Laboratory. Adhesion was measured by cross hatch adhesion test according to DIN 53151.

Procedures

(a) *Tetraglycidyl ether of 2,2, 6,6-tetramethylolcyclohexanol (resin A)*: 110 g (0.5 mol) of tetramethylolcyclohexanol and 15 g of a 50% aqueous solution of tetramethylammonium chloride were dissolved at 100°C in 1850 g (20.0 mol) of epichlorohydrin. The solution was cooled to 55°C and, by a lowering of the pressure to about 0.15 bar, a distillation of epichlorohydrin through a water separator was initiated. In the course of 3 h 220 g of a 50% aqueous sodium hydroxide solution (2.75 mol) were added dropwise, water being at the same

time continuously removed by distillation. After the separation of water was completed, distillation was continued for 1 h with the feeding back of epichlorohydrin, the reaction mixture was then cooled to 30°C, and the precipitated sodium chloride was removed by filtration and washed with epichlorohydrin. The combined epichlorohydrin solution was washed with 150 mL of a 10% aqueous NaH_2PO_4 solution; then with water and dried over Na_2SO_4 . The epichlorohydrin was distilled off in a rotary evaporator and the residue dried at 140°C at 0.02 bar to afford 192 g (86% of theory) of a viscous resin (epoxide content: 7.3 eq/kg).

(b) *Tetraglycidyl ether of 2,2, 6,6-tetramethylcyclohexanol (resin B)*: tetramethylcyclohexanol [225 g (1.02 mol)] was suspended in 410 mL of dioxane; 18 g of stannic chloride were then added and the temperature was raised to 100°C in the course of which a homogeneous solution was formed. Epichlorohydrin [564 g (6.1 mol)] was added dropwise, with stirring, in such a manner that the solution always gently boils. The solution was refluxed afterwards for 2 h; the dioxane was then distilled off and the residue dissolved in 1250 mL of toluene.

This solution was distilled under a reduced pressure of about 0.15 bar through a water separator and, over the course of 5 h, 396 g of a 50% aqueous sodium hydroxide solution (4.95 mol) were added dropwise at 55°C, water being continuously removed during this process. After the addition of the sodium hydroxide solution has been completed, the azeotropic distillation was continued for 30 min. The solution was cooled to 25°C, and washed with water and then with a 5% NaHSO_4 solution. The reaction mixture was dried over Na_2SO_4 ; the toluene was distilled off under reduced pressure to give 440 g (98% of theory) of a viscous resin (epoxide content: 7.4 eq/kg).

(c) *Cyclohexanone-formaldehyde condensation (CF resin)*: Distilled cyclohexanone [196.3 g (2 mol)] and water (30 mL) were mixed at room temperature. The pH of the solution was maintained during the reaction to pH 12 with a 50% aqueous sodium hydroxide solution using an Ismatec pump. The reaction mixture was heated to 70°C and 441.6 g (5 mol) of 34% aqueous formaldehyde were added dropwise over a period of 3 h. The reaction was continued for an additional hour. The mixture was cooled to 25°C, dissolved in 1 L ethyl acetate, washed three times with 200 mL ice water, and dried over Na_2SO_4 . The solvent was then distilled off in a rotary evaporator and the product was dried at 140°C at 0.02 bar to afford 229.05 g of a colorless solid resin.

\bar{M}_n : 575, \bar{M}_w/\bar{M}_n : 1.37

Hydroxyl content: 6.08 eq/kg

Softening point: 126°C

(d) *Etherification of the CF resin with epichlorohydrin (ECF resin)*: CF resin (100 g) prepared according to the procedure (c) and 2.4 g of a 50% aqueous solution of tetramethylammonium chloride were dissolved at 50°C in 382.6 g (4.15 mol) of epichlorohydrin. Distillation of epichlorohydrin through a water separator was initiated by reducing the pressure to about 0.15 bar. In the course of 2 h, 53.5 g of a 50% aqueous sodium hydroxide solution (0.67 mol) were added dropwise while removing water continuously by distillation.

After the separation of water was complete, heating was continued for an additional 2 h while feeding back the epichlorohydrin. The reaction mixture

was then allowed to cool to room temperature. The sodium chloride precipitated was removed by filtration and extracted with epichlorohydrin. The combined epichlorohydrin solution was washed with 120 mL of 10% aqueous NaH_2PO_4 solution, then with water, and dried over Na_2SO_4 . The epichlorohydrin was distilled off in a rotary evaporator and the residue dried at 140°C at 0.02 bar for 20 min to afford 92.9 g of a slightly yellow solid resin.

\bar{M}_n (GPC): 986, \bar{M}_w/\bar{M}_n : 3.31

Epoxide content: 3.58 eq/kg

Softening point: 89°C

IR (KBr, strong absorbances (cm^{-1}) = 910, 1065, 1100, 1250, 1450, 1705
2860, 2920, 3450

(e) *Preparation of a hydroxyl-terminated polycycloacetal (PCA) resin:* Hypophosphorous acid (0.3 g) was added to a suspension of 90 g (0.41 mol) of tetramethylolcyclohexanol in 600 mL of toluene. The mixture was heated to 85°C and 68 g of a 50% aqueous solution of glutaraldehyde (0.34 mol) were added dropwise over a period of 30 min. The solution was distilled under a pressure of about 0.15 bar through a water separator. When the separation of water was complete, reflux was continued at 1 bar for 2 h. The solution was allowed to cool to room temperature and the toluene was decanted from the resinous residue, which was dissolved in 400 mL of methanol and filtered. The solvent was distilled off in a rotary evaporator and the residue was dried at 120°C at 0.02 bar to give 119 g of a colorless solid resin:

\bar{M}_n : 1247, \bar{M}_w/\bar{M}_n : 2.08

Hydroxyl content: 7.29 eq/kg

Softening point: 131°C

IR [KBr, strong absorbances (cm^{-1}) = 890, 915, 1025, 1045, 1190, 1360
1400, 1450, 2860, 2930, 3400

RESULTS AND DISCUSSION

Liquid Epoxy Resins Based on TMCH

Figures 1 and 2 show the gel permeation chromatograms of TMCH—polyglycidylethers obtained by the one-step (resin A) and by the two-step process (resin B) respectively. Molecular weights derived from the GPC curves and other analytical data are shown below:

Resin	A	B
\bar{M}_n	650	450
\bar{M}_w/\bar{M}_n	1.7	1.044
Epoxide equivalent weight	137	135
Functionality (\bar{M}_n/EEW)	4.74	3.33
Epoxide content (eq/kg)	7.30	7.40
Hydroxyl content (eq/kg)	2.30	2.70
Chlorine (%)	0.75	6.44
Viscosity at 25°C (Pa s)	5.90	2.61
Color index (G & H)	3	1-2

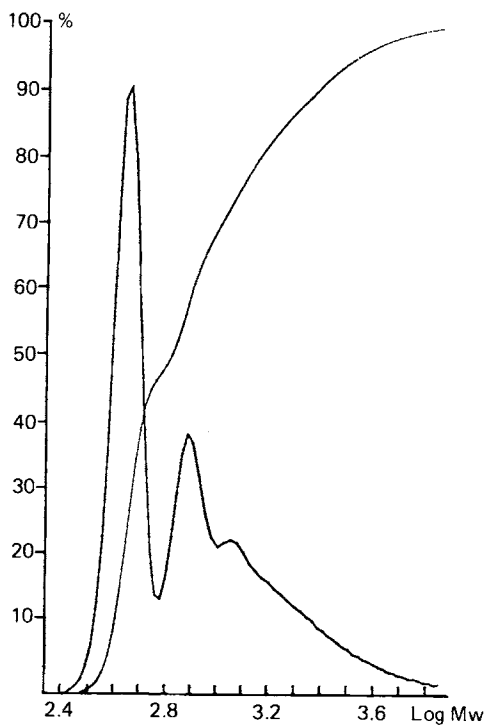


Fig. 1. Gel permeation chromatogram of tetraglycidylether of 2,2, 6,6-tetramethylcyclohexanol (resin A) obtained by the one-step process.

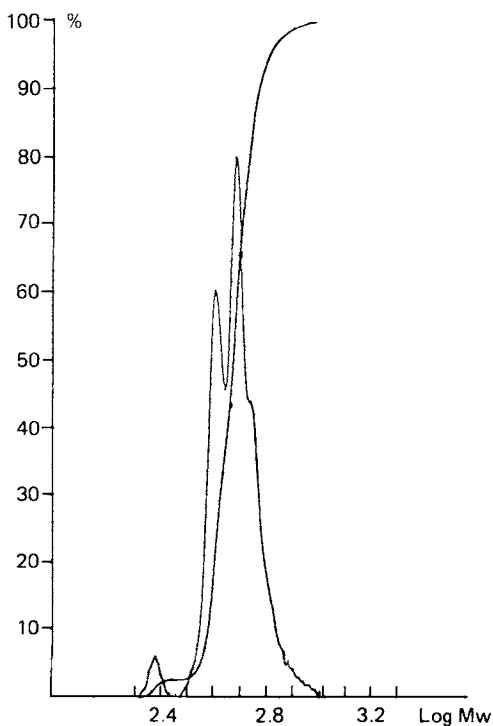
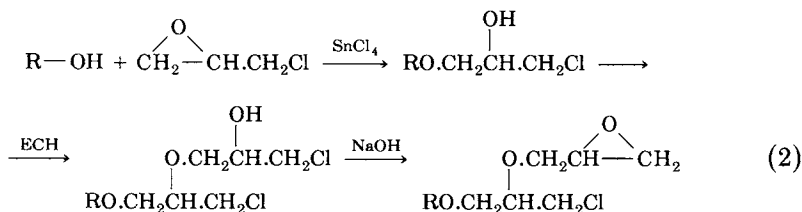


Fig. 2. Gel permeation chromatogram of tetraglycidylether of 2,2, 6,6-tetramethylcyclohexanol (resin B) obtained by the two-step process.

Resin A is higher in molecular weight than B; the latter corresponds almost to the calculated value (444), although it has a four-modal molecular weight distribution which may be due to different steps of etherification with ECH. This difference can be explained by methylol polycondensation under the alkaline conditions of the one-step process, leading in addition to higher molecular weight material. In contrast to this, the Lewis acid catalyst (SnCl_4) does not catalyze the methylol polycondensation to a noticeable extent (resin B).

The two processes result in resins with almost the same epoxide content and equivalent weight; however, the higher molecular weight resin A has a significantly higher functionality, which is an advantage for the cure and for several applications. The calculated hydroxyl content of the TMCH-tetra-glycidyl ether is 2.25 eq/kg. Resin A has practically the same value, which indicates that the secondary, sterically hindered hydroxyl group on the cyclohexane ring is not etherified by epichlorohydrin. This is in agreement with our general experience that the phase transfer process is not suitable for the glycidylation of secondary hydroxyls. In the presence of Lewis acids epichlorohydrin can be added to *sec* hydroxyls; however, much slower than to primary OH groups. In addition *sec* OH groups are generated by the addition process itself, which are subject to further reaction with epichlorohydrin in accordance to the following reaction scheme:



This mechanism results in a significant amount of so-called nonhydrolyzable chlorine, which is difficult to remove by treatment with caustic soda (resin B).

Due to its higher molecular weight and \bar{M}_w/\bar{M}_n ratio, resin A is higher in viscosity than resin B. Both types are only slightly colored and useful for the formulation of solvent free coatings and for the manufacture of castings and composites.

Coatings

One hundred grams of resin A and B, respectively, were mixed with 125 g of the polyaminoamide curing agent XU 283, having the following characteristic properties:

Amine content	2.0–2.25 eq/kg
Viscosity at 25°C	3.0–6.5 Pa s
Solids	100%
Color value according to Gardener and Holt	12

The above curing agent was also mixed with Araldite 6010 (formulation C).

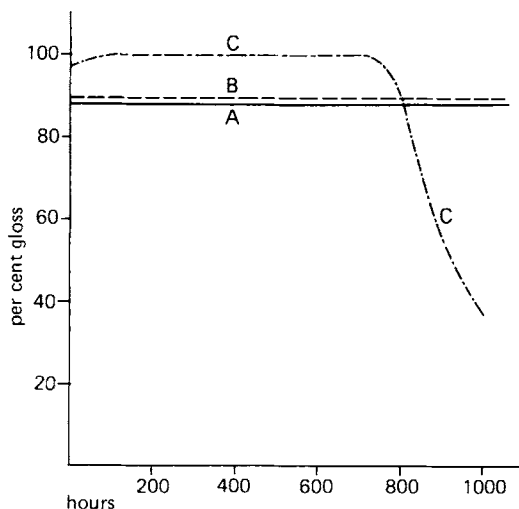


Fig. 3. Weatherometer tests on coatings A, B, and C obtained by hardening resin A, resin B, and Bisphenol A diglycidylether with XU 283.

The three coatings were applied to cold-rolled steel plates and cured during 7 days at 25°C. Clear, colorless, tough and strongly adhering films were obtained and then exposed during 1000 h in a xenon-arc weatherometer. Gloss retention and microcracking were observed in 100 h intervals. The results are summarized in Figure 3. Although the formulation C exhibited maximum initial gloss, which was maintained during a 700 h exposure, a dramatic loss of lustre took place, which was associated with an increasing occurrence of microcracks. After the 1000 h artificial weathering period the coating C made from the Bisphenol-A-based resin was entirely degraded. In contrast to this no decrease in gloss, no microcracks were observed on coatings A and B made from TMCH based cycloaliphatic epoxides.

Coatings A and C, and for comparison a polyurethane coating were exposed to the Florida climate and observed during 2 years. The results are shown in Figure 4. We notice a rapid deterioration of the Bisphenol-A-based coating, whereas the TMCH-based retains more gloss than the PUR coating and has no microcracks after the 2 years weathering period in Florida.

Castings

The toughness of the films encouraged us to investigate in addition casting applications. Since the high chlorine content of resin B is undesirable in electrical and matrix applications, only resin A was chosen for this purpose. Castings were made from the following two formulations:

Formulation:	D	E
Resin A (g)	61.25	138.8
Hexahydrophthalic anhydride (g)	64.20	—
Benzyl-dimethylamine (g)	0.125	—
4,4'-Diamino-diphenylmethane (g)	—	49.5

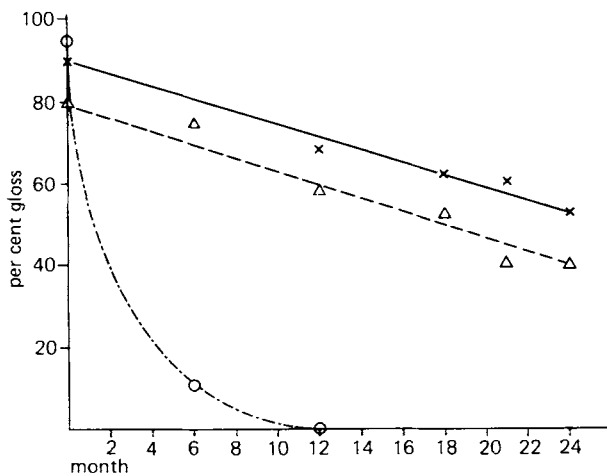


Fig. 4. Florida exposures of coatings A based on resin A(x—x), C based on Bisphenol A (O---O), and a polyurethane coating (Δ---Δ).

After cure for 2 h at 100°C, 2 h at 140°C, and 6 h at 180°C clear and tough plates (D = colorless, E = yellow) were obtained. Lap shear joints on an anticorrosive Al sheet were made in addition and cured under the above conditions. The mechanical and electrical properties of the castings are shown in Table I. Data from Table I show satisfactory mechanical properties, remarkably high glass transition and heat distortion temperature in particular for the aromatic amine cured formula E. This is unusual for a coating material and due to the high functionality of resin A ($\bar{F}_n = 4.72$).

Formulation D appears most useful for the manufacture of electrical insulators for outdoor use. The hexahydrophthalic cure would give rise to weather-

TABLE I
Mechanical and Electrical Properties

Property	Unit	D	E
Flexural strength	N/mm ²	108.2	107.7
Flexural elongation	%	4.85	5.2
Impact strength	kJ/m ²	10.7	19.5
T_g	°C	180	> 300
Heat distortion temp	°C	158	237
Water absorption during 4 days 25°C	%	0.40	0.69
1 h 100°C	%	0.30	0.55
Lap shear strength	N/mm ²	6.6	6.3
Volume resistivity at 25°C	Ω cm	4.2×10^{15}	2.7×10^{15}
at 100°C	Ω cm	3.6×10^{14}	2.0×10^{14}
at 200°C	Ω cm	3.5×10^{11}	4.2×10^{11}
Dielectric constant* at 25°C		4.1	5.8
at 100°C		4.4	6.4
at 160°C		4.6	6.4
Power factor* at 25°C	%	1.22	1.89
at 100°C	%	0.51	1.00
at 160°C	%	3.10	2.10

* Frequency 50 Hz.

TABLE II
Solid CF Resins

Molar ratio F/CH ^a	NaOH (wt%) on CH	\bar{M}_n	\bar{M}_w, \bar{M}_n	OH (eq/kg)	Softening point (°C)
1.6	3.88	962	2.56	3.11	140
2.0	3.88	798	2.94	4.03	140
2.2	3.88	811	1.92	5.19	122
2.5	3.88	663	1.52	6.23	126
pH ^b					
2.5	9	456	1.20	4.43	68
2.5	10	513	1.27	6.17	76
2.5	11	679	1.55	6.40	126

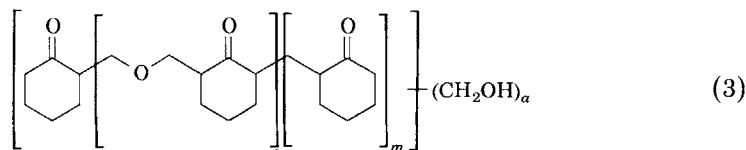
^a Formaldehyde/cyclohexanone.^b pH-static preparation with intermittent feed of aqueous caustic soda.

ability at least as good as the coating formulation with the hardener XU 283. Additional benefits are high volume resistivity and low power factor.

Solid Cyclohexanone-Formaldehyde (CF) Resins

Pure and crystalline TMCH can be obtained with a high amount of formaldehyde (5 mol/mol cyclohexanone) and under very mild and well-defined reaction conditions (CaO as catalyst).¹² Lower amounts of formaldehyde, higher reaction temperature, prolonged reaction time, and higher pH value give rise to the formation of solid resins. They are almost colorless, clear and brittle and somewhat resemble phenol formaldehyde novolacs. Table II shows some properties of these resins. We were particularly interested in the range 1.5–2.5 of the molar ratio, because high hydroxyl values plus high softening points can be obtained in that area. There is sufficient OH capacity for etherification with epichlorohydrin yielding ECF resins with softening points $\geq 80^\circ\text{C}$, which are useful for powder coating applications.

At the above low molar ratios there is not sufficient formaldehyde to reduce all carbonyl groups of cyclohexanone. The infrared spectrum of such a resin (Fig. 5) shows a strong carbonyl absorption at 1703.6 cm^{-1} . Masohiro¹¹ proposed the following schematic structure for CF resins:



According to the above formula, carbonyl reduction does not occur; similar to phenolic resols,¹⁴ formaldehyde forms methylene and dimethylene ether linkages between the cyclohexanone nuclei and in addition reactive methylol groups. Using the equation¹¹ with ϕ = oxygen content of the resin as obtained by elemental analysis, the cyclohexanone functionality F_c

$$F_c = \frac{1}{86} \left(\bar{M}_n - \frac{30}{16} \bar{M}_n \phi + 12 \right) \quad (4)$$

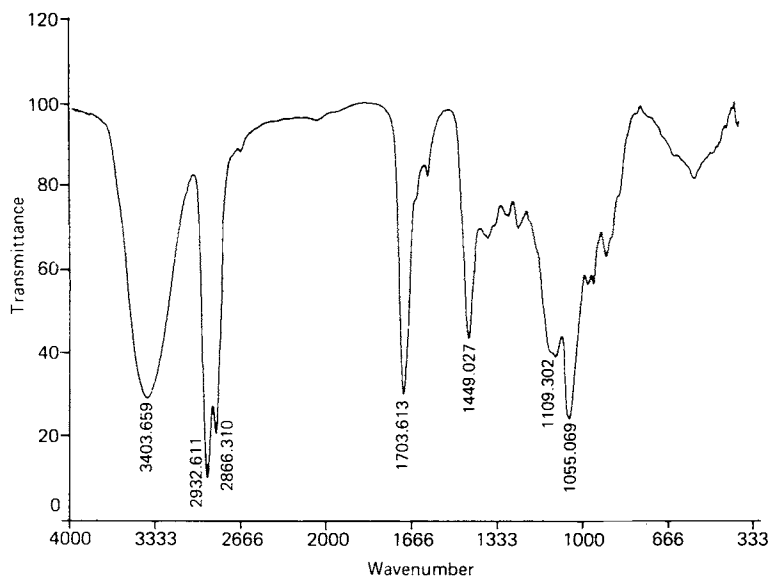
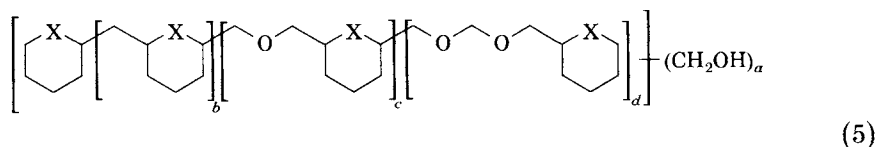


Fig. 5. Infrared spectrum of the CF resin obtained according to the procedure c.

of several resins has been calculated and compared with the analytical carbonyl content. Data of Table III shows that F_c exceeds considerably the carbonyl content. The differences (Δ) between these two quantities may be due to substituted cyclohexanol rings formed by the reduction of cyclohexanone rings with formaldehyde (cross Cannizzaro reaction) in a similar way as during the formation of TMCH. Unfortunately, we were unable to find or to develop a reliable analytical method for the determination of secondary hydroxyls in the presence of methylol groups. Taking into account the Δ values, we suggest to modify Masohiro's formula (4) in the following sense:



$$b + c + d \leq 10 \quad \text{X} = \text{C}=\text{O}; \text{CH}-\text{OH}$$

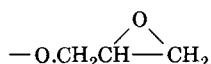
TABLE III
CF Resins: 2 h, 80°C, 0.08 mol NaOH

F/CH	Oxygen content \varnothing	\bar{M}_n	\bar{M}_w/\bar{M}_n	F_c	Carbonyl content (eq)	Δ (eq)
1.6	0.2037	920	2.53	7.26	3.22	4.04
1.6	0.2109	1050	3.16	8.08	2.99	5.09
2.2	0.2317	800	1.92	5.88	2.00	3.88
2.2	0.2345	810	1.82	5.75	1.76	3.99
2.5	0.2425	780	1.87	5.47	1.53	3.94

Glycidylethers of CF Resins

CF resins are soluble in epichlorhydrin and can be etherified by using the one-step phase transfer process (see procedure d). In Table IV properties of three CF resins, which have been used as starting materials and of the resulting ECF resins are listed.

We notice an increase in molecular weight, upon etherification with ECH, which is more than the replacement of the —OH by



group. This may be due to a type of advancement reaction of glycidyl ether groups with hydroxyls not yet etherified. We notice further a residual hydroxyl content due to secondary hydroxyls in the cyclohexanol nuclei. This is in accordance with our previous experience with the phase transfer process. We found that primary hydroxyls (methylols) react about 100 times faster with ECH than secondary hydroxyl groups do. As shown above, the secondary hydroxyl group of TMCH also remained unchanged upon reaction with ECH.

The ECFs are solid, brittle, low colored resins. Due to their multifunctionality resulting from epoxy and hydroxyl groups, their high reactivity, and their high softening points, they are useful for the manufacture of powder coatings. Such formulations and the properties of drycoats are shown in Table V and compared to drycoats made from a glycidylether of a polycycloacetal (EPCA), which is described below and to triglycidyl-isocyanurate, a state-of-the-art crosslinker for carboxyl terminated saturated polyesters.

Formulation no. 1 exhibited a sluggish cure resulting in a hard but brittle coating with insufficient solvent resistance. Catalyst addition [formula (2)] speeded up the cure considerably, and improved the impact test to a certain extent, the film elasticity, and the resistance towards methyl-ethyl ketone; however, we observed the same severe yellowing upon cure. This drawback is attributed to the presence of carbonyl groups. Since a further improvement of

TABLE IV
Properties of CF and ECF Resins

CF resin	A	B	C
\bar{M}_n	469	811	635
\bar{M}_w/\bar{M}_n	1.34	1.92	1.50
Hydroxyl content (eq/kg)	8.03	5.19	6.79
Softening point (°C)	80	132	123
Yield of ECF resin (phr)	89.4	112.8	110.7
\bar{M}_n	924	1284	1309
\bar{M}_w/\bar{M}_n	3.54	3.85	6.92
Epoxide content (eq/kg)	2.96	2.40	2.75
EEW	378	417	364
Functionality (\bar{M}_n/EEW)	2.73	3.08	3.60
OH content (eq/kg)	2.44	1.93	2.03
OH equivalent weight	410	518	493
OH functionality	2.25	2.48	2.65
Etherification (%)	54.8	55.4	57.5
Softening point (°C)	97	135	104

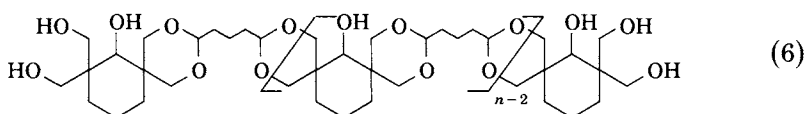
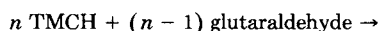
TABLE V
Powder Coatings 2 ± 0.2 Mills on Cold Rolled Steel Cure: 20 min at 200°C

Formulation	1	2	3	4	5
ECF resin (g)	15.4	15.4	—	—	—
EPCA resin D (g)	—	—	12.9	15.1	—
Araldite PT 810 (g)	—	—	—	—	5
Arakote 3003 (g)	54.6	54.6	57.1	54.9	65
TiO ₂ pigment (g)	28.5	28.15	28.5	28.5	28.5
Flow aid (g)	1.5	1.5	1.5	1.5	1.5
P catalyst (g)	—	0.35	—	—	—
Gel time at 200°C (s)	102	12	37	35	55
60° gloss (%)	82	72	74	84	90
Reverse impact (in. lb)	10	60	80	160	160
1/8 in. Mandrel bend	Fail	Pass	Pass	Pass	Pass
MEK double rubs	100	> 200	120	> 200	> 200
Adhesion	Exc.	Exc.	Exc.	Exc.	Exc.
Pencil hardness	H	H	H	H	H
Yellowness index	23	24	2	1	2

the film impact strength could not be achieved by means of formulation, we decided to make a drastic change of the resin structure by

- elimination of carbonyl groups
- attachment of terminal instead of lateral epoxy groups to the polymer backbone.

We used TMCH as starting material, which is entirely free from carbonyl, and built up linear polymers by condensation with dialdehydes, e.g., glutaraldehyde (Table VI) according to the following equation:



The highest melting PCA was etherified with 5 moles ECH per OH equivalent in the presence of tetramethyl-ammoniumchloride as phase transfer catalyst in analogy to procedure d of the experimental part.

TABLE VI
Polycycloacetals

n (excess TMCH/mol dialdehyde)	\bar{M}_n	\bar{M}_w/\bar{M}_n	OH content (eq/kg)		Softening point (°C)
			Calcd	Found	
1	590	1.46	11.90	12.04	77
0.8	654	1.51	9.98	11.49	92
0.5	780	1.66	8.94	9.78	111
0.1	1450	3.61	6.90	7.10	139

An EPCA resin was obtained in a 104% yield calculated on TMCH glutaraldehyde resin, which exhibited the following properties:

\bar{M}_n	2127
\bar{M}_w/\bar{M}_n	7.09
Epoxide content (eq/kg)	3.10
Epoxy equivalent weight	322
Functionality (\bar{M}_n /EEW)	6.60
Hydroxyl content (eq/kg)	4.30
Hydroxyl equivalent weight	232
Hydroxyl functionality	9.15
Chlorine (%)	0.51
Softening point (°C)	86

We notice again a considerable increase in \bar{M}_n and polymolecularity upon reaction with epichlorohydrin. This multifunctional solid EPCA resin (referred as resin D in Table V) has been used to formulate powder coatings (nos. 3 and 4). They exhibit fast gelation without catalyst and hard, strongly adhering and MEK resistant films are obtained, which do not yellow upon baking. The structural modification of the novel epoxy resins based on cyclohexanone-aldehyde condensation products—i.e., terminal pairs of epoxide groups instead of lateral ones—resulted in an excellent toughness (reverse impact strength = 160 in. lb for formulation no. 4) and roughly in an overall match of the standard formulation no. 5. It can be concluded that the above-described EPCA resin is a crosslinker for carboxyl-terminated polyesters of similar usefulness in powder coatings than the crystalline triglycidyl-isocyanurate.

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