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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Curing of Aqueous Epoxy Dispersions in the Presence of a Cycloaliphatic Amine

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Abstract—The possibility of using a cycloaliphatic amine NC-558 as a curing agent for water-based epoxy compounds was examined. The effect of the component concentrations and temperature on the properties of the films obtained was studied.

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Enamels based on organosoluble epoxy oligomers (EOs) are widely used in paint-and-varnish industry for preparing high-quality corrosion-resistant and chemically stable coatings [1]. These enamels are toxic, inflammable, and dangerously explosive because they contain organic solvents. They negatively affect the human health and the environment. Today a new generation of water-dispersible systems came into use in the world practice: aqueous dispersions (ADs) of various oligomers and polymers, so-called artificial latexes [1, 2]. Aqueous dispersions of EOs can be used as alternative to the above solvent-based enamels for the protection of construction steel and of wood and concrete items. Coatings formed from EO ADs show better service characteristics than those prepared from synthetic latexes and approach coatings prepared from solutions of epoxy resins in organic solvents. Therefore, such coatings attract growing attention of specialists and find steadily expanding use in building, mechanical engineering, and radio electronics [3–5]. The advantages of coatings formed from EO ADs are as follows [1]: resistance to chemicals, improved mechanical properties, low absorption of contaminants by the surface, high adhesion to various types of supports, high interlayer adhesion, good external appearance, and high weather resistance.

Successful development of paint-and-varnish protective materials based on EO ADs depends not only on the quality of dispersions themselves, but also on the nature of curing agents and on other conditions of coating formation.

In this study we examined the possibility of using NC-558 cycloaliphatic amine as a curing agent for water-based epoxy compounds and studied how the component concentrations and temperature affect the properties of the films obtained.

EXPERIMENTAL

In our study we used an EO AD of the oil-in-water type with 60% content of the dispersed phase. The aqueous dispersion was obtained by direct emulsification of EO in the presence of a nonionic surfactant and a stabilizer [4]. As EO we used liquid ED-20 epoxy–4,4'-isopropylidenediphenol resin containing 20.0% epoxy groups, with the molecular weight Mn = 500 [GOST (State Standard) 10687–84] [2]. The characteristics of the ED-20 AD obtained are given below.

External appearance	Milky white liquid
Weight fraction of nonvolatile substances, %, no less than	63.0 ± 1
Viscosity at 20°C (outflow time from VZ-4 viscometer, s, at orifice diameter of 4 mm)	34
pH	7.5
Density, kg cm^{-3}	1092
Surface tension, 10^3, J m^{-2}	40.0
Mean particle size, μm	1–5

As a curing agent for the experimental compounds we chose NC-558 cycloaliphatic amine hardener

(Cardolite) used in industry for curing organosoluble epoxy materials. The characteristics of NC-558 are as follows:

External appearance	Amber-colored liquid
Viscosity	900
Density, kg cm^{-3}	0.98
Amine content, mg KOH/g	360

The curing agent consists of aliphatic polyamines linked to the aromatic framework of 3-*n*-pentadecadienylphenol by a side aliphatic chain. The compositions of the compounds are given in Table 1. All the compounds are nontransparent creamy liquids.

The spreadable life of the compounds was evaluated from changes in their viscosity in the course of storage at 20°C. The viscosity of the compounds was determined according to GOST (State Standard) 8420–74. Free films were obtained according to GOST 14243–78.

The curing kinetics was monitored by variation of the content of the gel fraction (fraction insoluble after cross-linking). The gel fraction content was determined by extraction of the soluble fraction with acetone in a Soxhlet apparatus for 24 h.

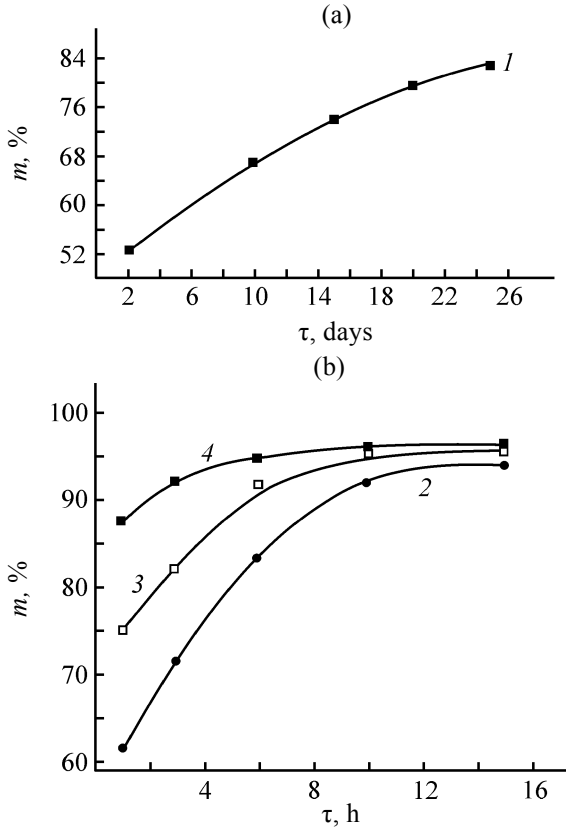

Fig. 1. Content m of insoluble gel fraction in films cured at (*1*) 20, (*2*) 70, (*3*) 80, and (*4*) 140°C, as a function of the curing time τ.

The curing process was monitored by IR spectroscopy. The IR spectra of the samples were taken with an FTIR M 2000 Series Fourier Transform IR spectrometer (MIDAC, USA) in the wavenumber range 400–4000 cm^{-1}, with a resolution of 4 cm^{-1}. The spectra were processed with Grams/32 program (Galactic, USA).

Differential thermal analysis was performed with a Netzsch STA 409 PC/PG device at a heating rate of 1 deg min–1 in an argon atmosphere, with a sample weight of 57.3 mg. The microstructure of the samples was examined by scanning electron microscopy with a LEO 1420 device. The sample surface was coated with gold by vacuum sputtering on a VUP-2K unit. The water absorption of the films was determined by the weight gain of the film samples on their keeping for various times in a desiccator with 99% humidity [6]. The weather resistance of the films was evaluated after 15 cycles of their freezing to –20°C and subsequent heating in an oven to +50°C. The relative hardness of the films was determined with a 2124 TML pendulum device according to GOST 5233–89, and the adhesion, by the grid notching method according to GOST 16253.

The films were cured at 20°C for 2, 5, 10, 15, 20, and 25 days (cold curing) and at 70, 80, and 140°C for 1, 3, 6, 10, and 15 h (hot curing). Studies showed that the curing agent is compatible with ED-20 AD and is readily and uniformly distributed in it. The presence of the curing agent increases the viscosity of compounds; therefore, its concentration in them is limited. For example, addition of the curing agent in an amount of 30 wt % (compound no. 4) and more increases the viscosity of the compounds and decreases its spreadable life. The viscosity of compound nos. 1–3 (outflow time) is 40–45 s, and the spreadable life, 1.5–2 days.

Preliminary tests showed that films formed from compound nos. 1 and 2 got hardened (lost stickiness) at 20°C in 10–15 days, and compound no. 3, in 2 days.

Table 1. Composition of compounds

Component	Content, wt %, in indicated compound			
	no. 1	no. 2	no. 3	no. 4
ED-20 AD	90	80	60	35
Curing agent	5	10	20	30
Distilled water	5	10	20	35

Therefore, compound no. 3, was chosen for further studies.

A study of the curing kinetics showed (Fig. 1, curves *2–4*) that, in the course of curing at 20°C, the gel fraction content increased slowly. The content of the insoluble fraction was 52.5% in 2 days, 67% in 10 days, 74% in 15 days, 79.5% in 20 days, and 83% in 25 days (Fig. 1, curve *1*). With increasing temperature, the curing rate increased. At 70°C, the content of the insoluble fraction was 61.7% in 1 h, 71.6% in 3 h, 83.3% in 6 h, 92% in 10 h, and 94% in 15 h; at 140°C, 87.5% in 1 h, 92% in 3 h, 94.8% in 6 h, 96% in 10 h, and 96.2% in 15 h. Thus, gelation is mainly complete (the content of the insoluble fraction reaches 94–96.3%) in 15, 10–15, and 6–15 h in the films heat-treated at 70, 80, and 140°C, respectively.

These data are well consistent with the results of measuring the film hardness (Fig. 2). The hardness of the films cured at 20°C for 2 days is low (0.05 unit). With increasing time of cold curing, the film hardness increases, reaching 0.15 unit in 10 days, 0.27 unit in 20 days, and 0.28 unit in 25 days. The plots of the film hardness vs. curing time at 70–140°C are ascending curves gradually flattening out (Fig. 2, curves *2* and *3*). The maximal hardness is attained at 70°C in 10 h (0.33 unit), at 80°C in 6 h (0.35 unit), and at 140°C in 3 h (0.38 unit). Longer curing at these temperatures does not lead to further increase in the film hardness.

The water absorption of films formed under various curing conditions is essentially different (Fig. 3). The water absorption of the films cured at 80 and 140°C is lower than that of the films obtained by cold curing. Longer curing of the films enhances their moisture resistance, which may be due to a change in the packing density in going to more severe hardening conditions.

Figure 4 shows the IR spectra of the curing agent and compound no. 3 before curing and after curing at 20°C for 25 days, at 80°C for 1 h, and at 80°C for 6 h. As can be seen, the spectrum of the uncured compound (spectrum 2) contains an absorption band with a maximum at 3431 cm^{-1}, belonging to vibrations of the hydroxy group ν(OH) and confirming the presence of water in the compound. The spectrum also contains absorption bands with maxima at 2972, 2967, and 2872 cm^{-1}, corresponding to CH_2 vibrations, and

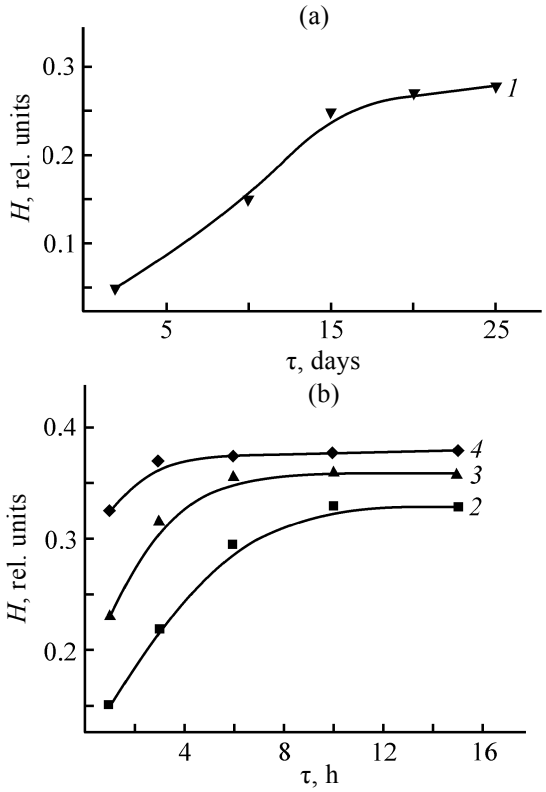

Fig. 2. Hardness *H* of films cured at (*1*) 20, (*2*) 70, (*3*) 80, and (*4*) 140°C as a function of curing time τ.

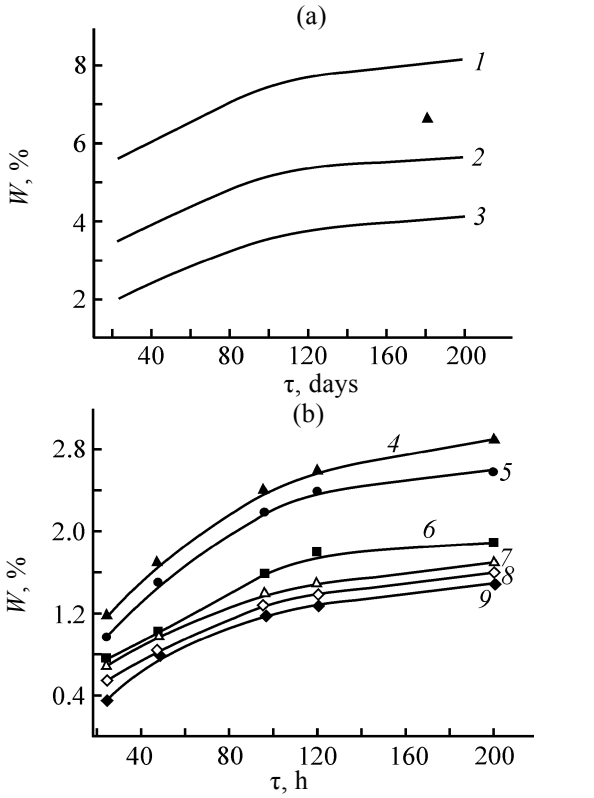

Fig. 3. Water absorption *W* of films as a function of testing time τ. Film curing temperature, °C: (*1–3*) 20, (*4–6*) 80, and (*7–9*) 140. Curing time: (*1*) 2 days, (*2*) 10 days, (*3*) 25 days, (*4, 7*) 1 h, (*5, 8*) 3 h, and (*6, 9*) 6 h.

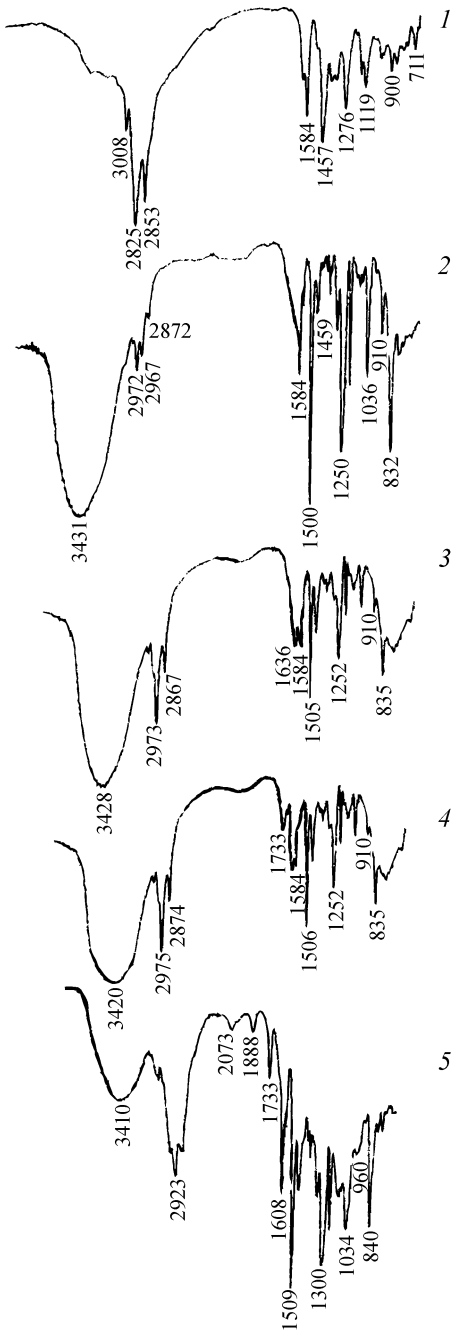

Fig. 4. IR absorption spectra (ν, cm^{-1}) of the (*1*) curing agent, (*2*) uncured compound no. 3, and (*3*–*5*) compound no. 3 cured (*3*) at 20°C for 25 days, (*4*) at 80°C for 1 h, and (*5*) at 80°C for 6 h.

a group of bending vibrations of the benzene ring at 1500 cm^{-1}. Absorption bands with maxima at 1250, 910, and 832 cm^{-1} are indicative of the presence of epoxy groups [7]. The most convenient band for monitoring chemical transformations of epoxy groups is that with a maximum at 910 cm^{-1}, as the remaining two bands overlap with absorption bands of other groups [7]. The curing agent NC-558 also absorbs in this region, but it has a characteristic band at 1584 cm–1 (Fig. 4, spectrum *1*) with which it is convenient to monitor its chemical transformations. As the curing involves the reaction of an epoxy group of the resin with an amino group of NC-558, the intensity of the absorption at 910 cm^{-1} can be taken as the measure of conversion.

Curing of the compound at 20°C for 25 days (Fig. 4, spectrum *3*) and at 80°C for 1 h (spectrum *4*) is accompanied by a decrease in the absorption intensity at 910 and 1584 cm^{-1}, due to a decrease in the concentrations of epoxy groups in ED-20 resin and of the curing agent in the compound. In the spectrum of the sample cured at 80°C for 1 h, a band appears at 1733 cm^{-1}, indicative of formation of an ester carboxy group. It should be noted that the bands at 910 and 1584 cm^{-1} do not fully disappear upon cold and hot (80°C, 1 h) curing. This fact suggests that certain amounts of epoxy groups of ED-20 resin and of the curing agent remain unchanged in the cured compounds.

Curing of the same compound at 80°C for 6 h (spectrum *5*) is accompanied by an increase in the intensity of the absorption band with a maximum at 1733 cm^{-1} and appearance of bands with maxima at 2073 and 1888 cm^{-1} (carbonyl groups), owing to the reaction of the epoxy groups with the curing agent. The absorption bands at 910 and 1584 cm^{-1} fully disappear.

It should be noted that both cold and hot curing leads to a decrease in the intensity of the hydroxyl vibration bands ν(OH) and to their short-wave shift. A decrease in the content of hydroxy group in the course of curing may be due to the reaction of functional groups of the curing agent with hydroxy groups, with the formation of an aliphatic polyamine ether.

Analysis of the IR spectra confirms the data obtained from physicochemical tests: The films cured at 80°C for 6 h acquire fairly high hardness (0.37 unit) and moisture resistance (1.9%), in contrast to cold-cured films (Figs. 2, 3).

The derivatogram of ED-20 AD has five endothermic peaks with maxima at 45.3, 90.2, 93.3, 97.0, and 104.8°C, accompanied by a weight loss. As shown by thermogravimetric measurements, in the first step (20–50°C) the weight loss is 6.93%; in the second step (50–77°C), 5.50%; in the third step (77–88°C), 2.67%; in the fourth step (88–104.8°C), 7.36%; and in the fifth step (104.8–150°C), 7.3%. The total weight loss at 150°C is 29.76%. All the observed endothermic effects correspond to the release of water from the sample.

The DTA curve in the range 60–88°C shows a slight deviation from the straight line (+0.00091965 μV mg^{-1}) with a maximum at 77°C. Presumably, in this temperature range the epoxy resin gradually reacts with the curing agent. The reaction of the components in the course of curing the compound at 70–80°C is confirmed by a change in the content of the insoluble fraction (Fig. 1).

Figure 5 shows an electron micrograph of a film cured at 80°C for 6 h. As can be seen, the film surface is smooth, without defects caused by the presence of non-cross-linked segments of macromolecules.

The films cured at 80°C for 3–6 h and at 140°C for 1–6 h showed no changes in the external appearance after 15 cycles of freezing to –20°C and subsequent heating in an oven to +50°C, i.e., the films are weather-resistant.

As seen from Table 2, the adhesion of films formed on the surface of 03 kp steel strongly depends on the curing conditions.

An increase in the temperature and time of film curing leads to an increase in their adhesion to the metal support. Films cured at 80°C for 6 h or at 140°C for 1–6 h have a point 1 adhesion.

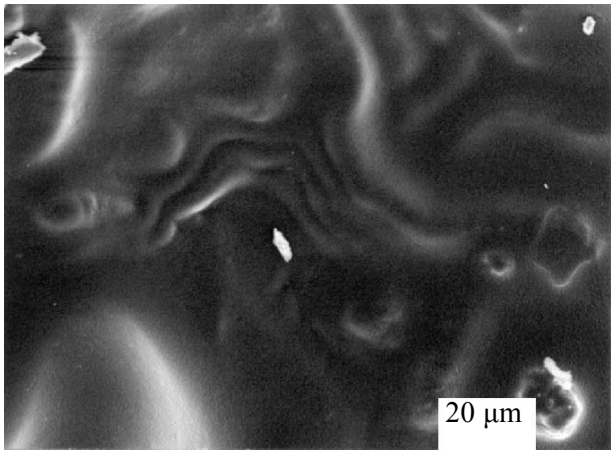

Fig. 5. Electron micrograph of the film cured at 80°C for 6 h.

CONCLUSIONS

(1) Cold curing of experimental films leads to a slow increase in the gel fraction content, from 52.5 to 83% in the period from 2 to 25 days. This is caused by hindered diffusion of curing agent molecules to microdroplets of the epoxy oligomer surrounded by a shell of an emulsifier and a stabilizer.

(2) With increasing temperature, the curing occurs more intensely. Upon curing the compound at 80°C for 6 h or at 140°C for 3 h, 96% of macromolecules of the epoxy oligomer are bound in a three-dimensional structural network. This leads to considerable enhancement of the hardness and to a decrease in the moisture permeability of the formed film.

Table 2. Adhesion of films to a metallic support

Curing temperature, °C	Curing time	Adhesion, point	Adhesion characteristic
20	2 days	3	Partial exfoliation of film along the lines of grid notches
	10 days	3	"
80	20 days	2	Partial exfoliation of film in the form of small flakes in sites of intersection of grid lines
	25 days	2	"
	1 h	2	"
	3 h	2	"
140	6	1	Notch edges are fully smooth, signs of exfoliation are observed in none of grid squares
	1 h	1	"
	3 h	1	"
	6 h	1	"

(3) Both epoxy and hydroxy groups of macromolecules of the epoxy oligomer participate in formation of a three-dimensional structure.

(4) In contrast to organosoluble epoxy oligomers, the spreadable life of compounds of an aqueous dispersoin of an epoxy oligomer with a curing agent is as long as 1.5–2 days, which makes this compound more convenient in application.

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