

<https://doi.org/10.3176/oil.1995.3.08>

DIGLYCIDYL ETHERS FROM SHALE OIL ALKYL RESORCINOLS

2. METHODS FOR PRODUCTION AND CHARACTERISTICS OF UNCURED ALKYL RESORCINOL EPOXY RESINS

E. RAIDMA

Oil Shale Research Institute
Kohtla-Järve, Estonia

Alkyl resorcinol epoxy resins (diglycidyl oligomers) are produced mainly from concentrates of 5-alkyl resorcinols extracted from shale oil water-soluble phenols.

Manufacture of epoxy resins is effected in two stages: synthesis of basic resins from alkyl resorcinols and additional treatment of ordinary resins for the purpose of making products with improved quality.

Characteristic data for uncured resins are given for the products with epoxide equivalent mass from 120 to 2000 g/mole. These materials include modified alkyl resorcinol epoxy resins from commercial production, low-viscosity alkyl resorcinol epoxy resins with improved quality, high-purity crystalline diglycidyl ethers of alkyl resorcinols and solid thermoplastic alkyl resorcinol epoxy resins.

Introduction

In the preceding paper [1], the resources and composition of shale oil alkyl resorcinols (AR), as the feedstock for the synthesis of diglycidyl oligomers (epoxy resins), were studied. That paper also presented structural formulae of the end- and by-products. Based on those results, and earlier studies [2], the regularities of the synthesis of AR epoxy resins of improved quality are discussed and characterized in detail.

Numerous references [3-7] have shown the potential for improving the quality and producing a larger assortment of commercial epoxy resins. Special attention has been paid to the heterogenous-phase method of synthesis using different catalysts and various application options. Methods for eliminating undesirable by-products, consideration of alternative feedstocks, and other parameters are also discussed. In all cases, the analytical testing of intermediate and end products is considered to be very important, especially the determination of their molecular mass distribution, functional character, and content of imperfect (defected) oligomers. The modification of epoxy materials, even of traditional ones, is also currently in progress [9, 10].

Production of Epoxy Resins from Concentrates of Shale Oil Based Alkyl Resorcinols

A convenient classical method of synthesis was applied [2, 8] for producing epoxy resins (diglycidyl oligomers - DO) from mixtures and concentrates of shale-derived alkyl resorcinols [1]. Water solutions of sodium hydroxide of varying concentration (5-45 %) served as a catalyst both for binding epichlorohydrin (ECH) to AR hydroxyl groups and for dehydrochlorination of reaction products. Lye solution was added to the reaction mixture with some excess.

For one mole of alkyl resorcinols, 2.05-4.0 moles of ECH are needed. The actual quantity depends on the desired viscosity and molecular mass of the end product. Synthesis of AR epoxy resins, e.g. of the types AREM-2 and AREM-5, are carried out using a modifier - a mixture consisting of hydroxy and alkyl derivatives of 1,3-dioxan and ethers. Dioxan alcohol, 4-methyl-4-oxyethyl-1,3-dioxan, is dominant in the product. Those by-products of dimethyldioxan production are delivered by synthetic rubber plants.

Commercial production methods for obtaining AR epoxy resins using the corresponding operating conditions were developed on a laboratory scale (sample size 150-400 g) and a pilot unit (reactor volume 15 l, sample size 2.5-3.0 kg). Epoxy resin AREM-2 was prepared on an industrial scale (sample size 2.5-2.8 tons). Additional purification may be carried out in smaller amounts (low-tonnage production).

The basic synthesis of liquid alkyl resorcinol epoxy resins, as produced at the Oil Shale Research Institute, consists of the following stages:

- preparation of feedstock solution;
- synthesis of epoxy oligomers (dosage of alkali);
- regeneration of the ECH excess;
- settling and separation of the resin salt solution and water;
- distillation of toluene (resin drying).

Commercial production of epoxy resins in RAS "Kiviter" is a continuous operation. Some individual units operate in a batch cyclic mode.

Several variables play essential roles in the production of epoxy resins with a desired molecular mass distribution and minimal content of imperfect (defected) molecules. These variables include ratios of initial reagents, their composition, and the stage of product formation. Laboratory investigations and pilot tests have shown that the right choice of alkyl resorcinol feedstock, suitable reaction medium (addition of a modifier), and optimal conditions for dosage of alkaline water solutions guarantee the attainment of the desired product.

We have established that it is practical to add NaOH water solutions to the reaction mixture according to an exponential correlation. This can be represented by a logarithmic dependence, $\log N = a + b \log x$, where N is the amount of NaOH and x is the time for its addition. Constants a and b are determined by production conditions and capacity. As a rule, in the

addition of ECH to AR, about 20 % of the total calculated dose of NaOH is added during the first step of synthesis. A more complete binding of epichlorohydrin to AR hydroxyl groups guarantees the formation of a low-molecular resin, e.g. of the type AREM-2-20Q.

The average structure of its molecule forms from 1.15 moles of AR and 2.15 moles of ECH. Also, the first stage of this addition reaction is highly exothermic ($Q = 110 \pm 10$ kJ and the maximum rate of heat release is about 100-150 W per a g-eq. of AR hydroxyl groups). This can lead to the superheating and boiling of the reaction mixture, especially in an industrial-scale production of epoxy resins. Passing through the maximum temperature (not exceeding 85 °C) during the first stage of the reaction promotes the formation of low-molecular resin and inhibits the rate of formation of imperfect molecules, especially of C-alkylation products.

It has been established that greater amounts of by-products are formed when a strongly oxidated (black) fraction of AR (295-320 °C) is used as the feedstock, and when toluene is present in the reaction medium, i.e. the design conditions of a heterogenous-phase synthesis have not been used. The high content of impurities in the reaction mixture impairs the conditions necessary for settling and separation of the salt solution (wash waters) from the organic layer. As a result, the losses increase, the quality of the end product becomes worse, and its subsequent treatment will be complicated. Consequently, when preparing basic alkyl resorcinol epoxy resins, all the process factors which could lead to an elevated content of impurities and molecules having defective functionality in the end product, should be avoided.

The principal route for manufacturing epoxy resins of the type AREM-2 (Fig. 1) includes the production of basic resins. These could be subjected to an additional purification step (clarification), if needed, using absorption of admixtures on activated charcoal and silica gel.

The production of low-molecular resins of higher quality (cleaned) (Fig. 2) is carried out by extraction with diisopropyl ether (resin AREM-2-20E) or by using vacuum distillation (AREM-2-28D). The latter produces a mixture of monomeric diglycidyl ethers of a very low viscosity ($\eta_{20^\circ} = 0.2-0.6$ Pa·s). Pure crystalline diglycidyl ethers are made from concentrates of 5-methyl resorcinol, 5-ethyl resorcinol or 2,5-dimethyl resorcinols in two stages (Fig. 3), as follows: at the beginning of the process, the crude initial resin is made by direct synthesis (with the end-product content of 70-75 %).

From this product, diglycidyl oligomer powder of 99 % purity (as determined by HPLC) is separated by vacuum distillation or crystallization from an alcoholic system. Residues remaining after separation of pure products represent medium-molecular epoxy resins (Figs. 2 and 3) with the epoxy group content of 18-20 %. Solid thermoplastic epoxy resins are made from epoxy resins and alkyl resorcinol concentrates according to a catalytic addition reaction (Fig. 4). A relatively colorless "phenoxy resin" of linear structure can be made from pure reactants prepared on 5-methyl resorcinol basis.

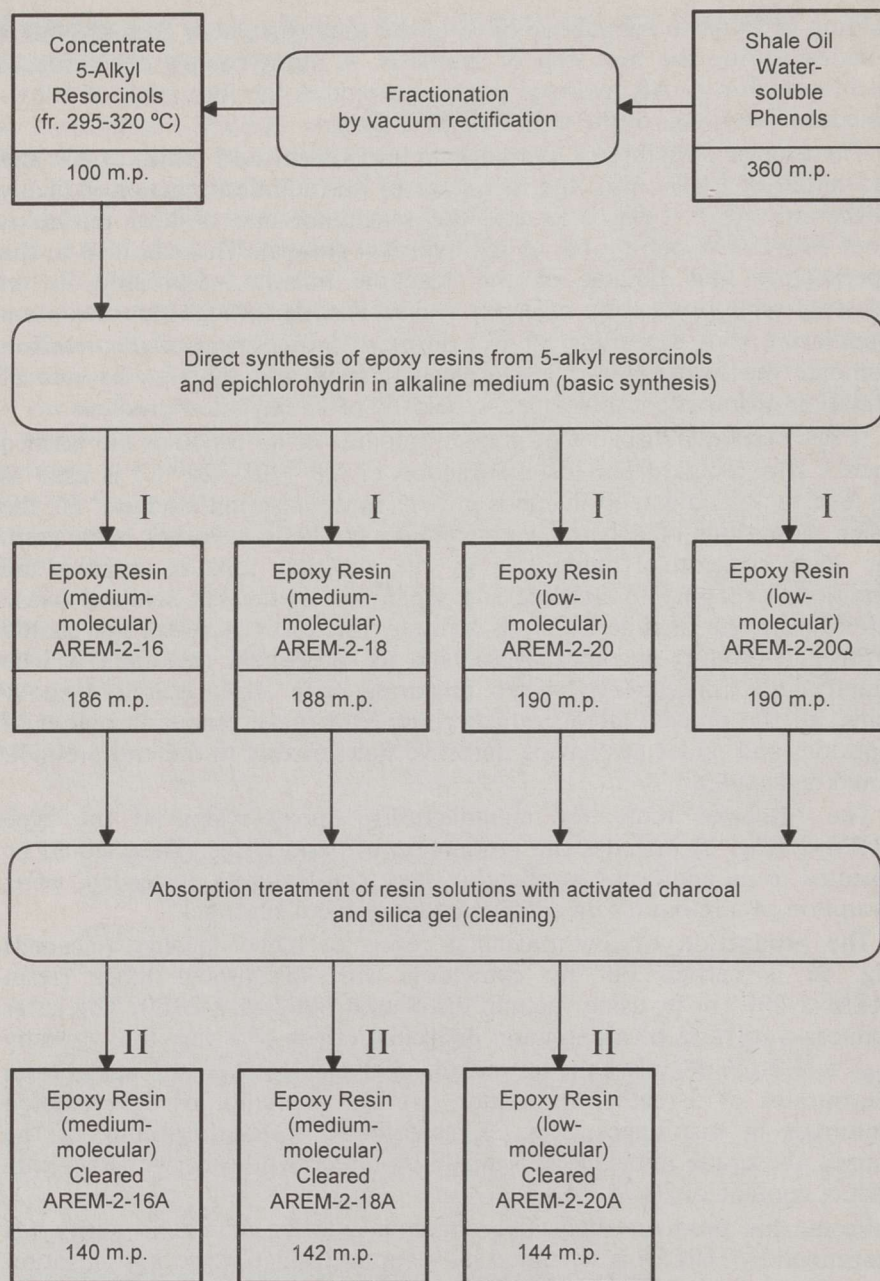


Fig. 1. Production of modified alkyl resorcinol epoxy resins type AREM-2: I - ordinary resins, II - resins with improved quality; m.p. - mass part, here and in Figs 2-4

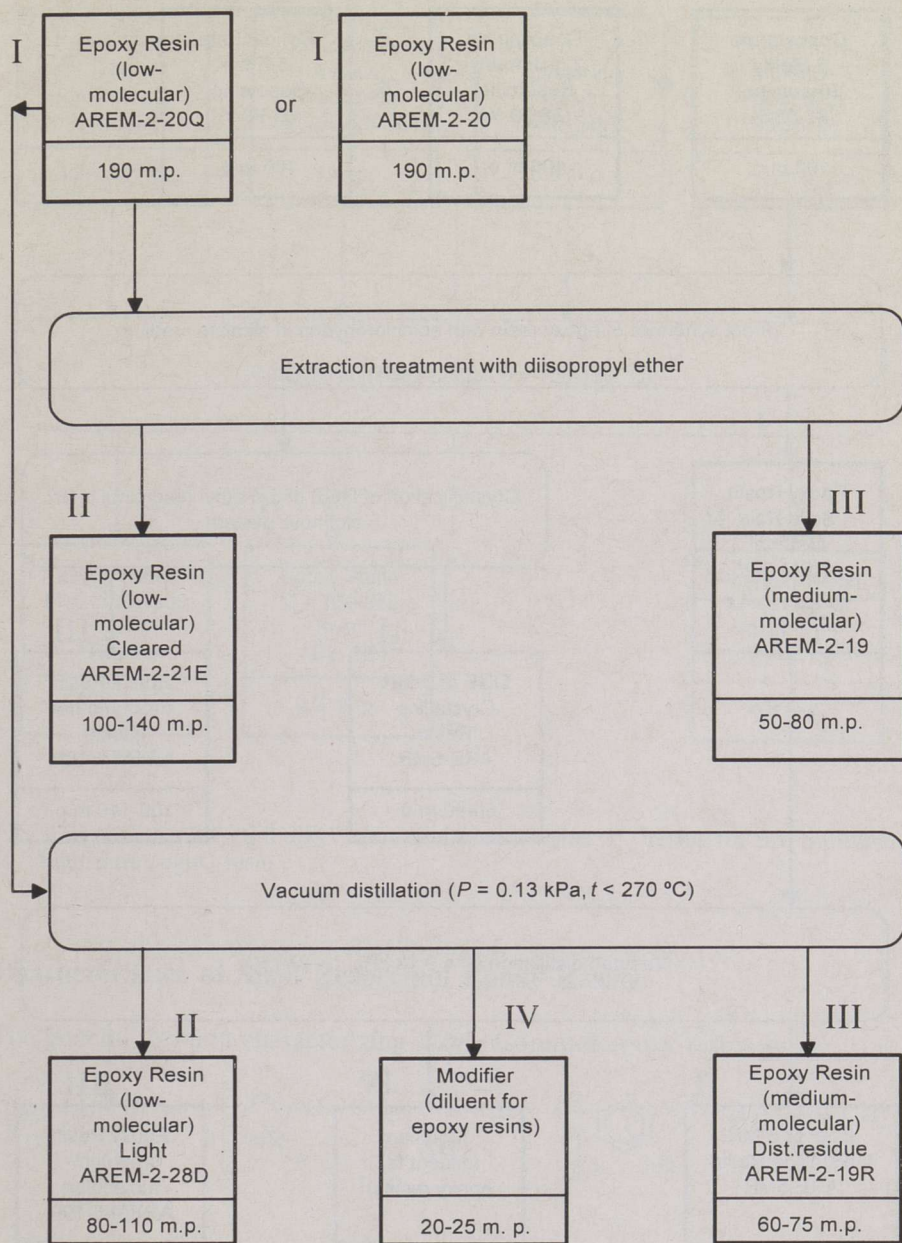


Fig. 2. Production of light (cleaned) alkyl resorcinol epoxy resins: I - ordinary resins, II - high pure (light) resins, III - residual resins, IV - modifier as diluent for epoxy composition

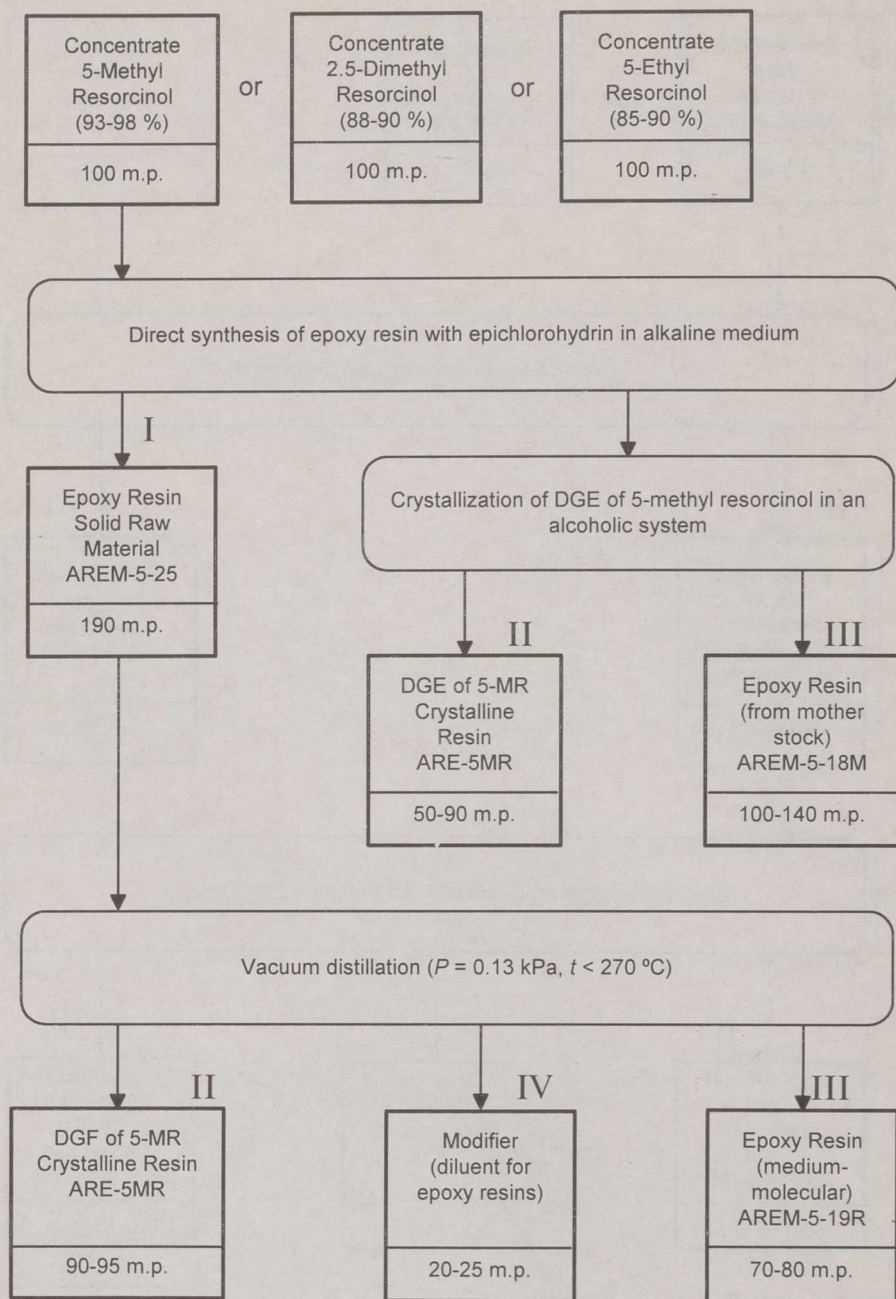


Fig. 3. Production of high-purity crystalline DGE of 5-methyl resorcinol (2,5-dimethyl resorcinol, 5-ethyl resorcinol): I - raw resins, II - crystalline DGE (high purity), III - residue resins, IV - modifier as diluent for epoxy compositions

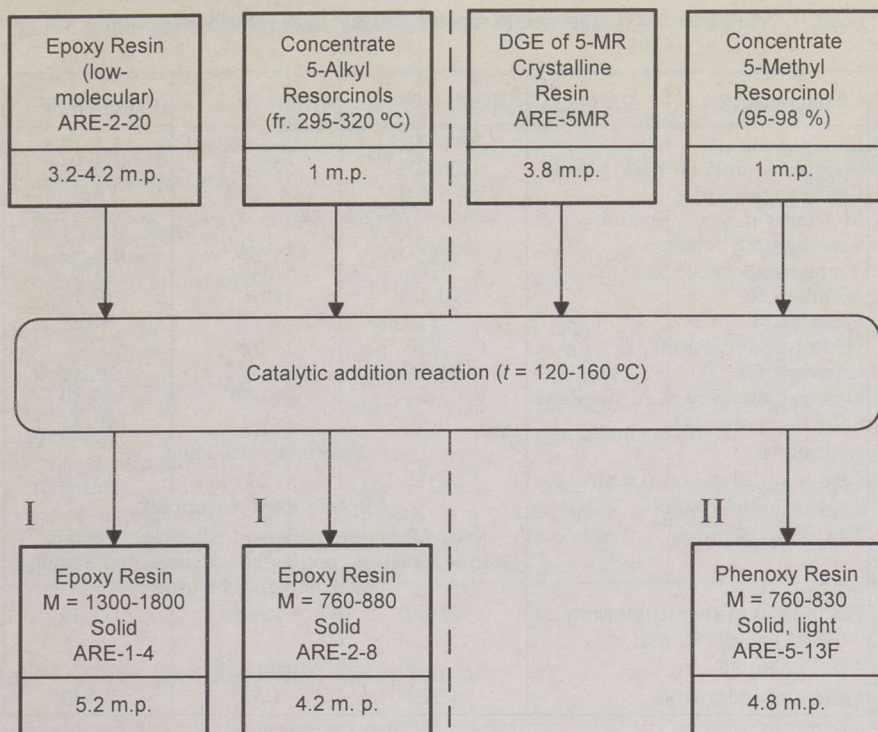
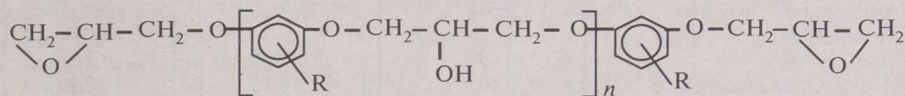


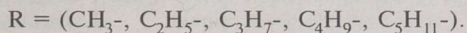
Fig. 4. Production of solid alkyl resorcinol epoxy resins: I - resins for tire industry, II - high pure (light) resin

Characteristics of Alkyl Resorcinol Epoxy Resins

The general formula characterizing alkyl resorcinol epoxy resins is:



where



The numerical values of coefficient n presented in Tables 1-4 characterize the molecular mass distribution range for a given type of epoxy resin.

The main characteristics of commercial epoxy resins of the type AREM-2 are given in Table 1. Technical standards and testing methods for these resins are specified in Estonian standard EVS 651:1994.

Table 1. Modified Alkyl Resorcinol Epoxy Resins Type AREM-2

Characteristics	AREM-2-20	AREM-2-18	AREM-2-16
Epoxy groups, %	19.0-21.5	17.5-19.0	15.5-17.5
Epoxide equivalent mass, g/mole	200-226	226-245	245-277
Epoxy value, eq/kg	4.5-5.0	4.1-4.4	3.6-4.1
Molecular mass distribution of diglycidyl ethers	$n=0/n=1/n=2$ ~30/2/1	$n=0/n=1/n=2$ ~10/2/1	$n=0/n=1/n=2$ ~6/2/1
Average molecular mass	320	340	370
Modifier, %	10-15	10-12	10-12
Volatiles, %	<2.0	<1.5	<1.0
Hydrolyzable chlorine, %	<0.4	<0.3	<0.2
Chlorine ions, %	<0.002	<0.003	<0.004
Dynamic viscosity at 20 °C, Pa · s	3-6	10-30	30-80
Softening point, °C	0-3	5-7	10-15
Appearance	Brown viscous liquid		
Degree of coloration (Gardner)	12-15	12-15	13-16
Type of initial phenol	Mixed 5-alkyl resorcinols		
Typical applications	Resins for two-component adhesives, sealants, flooring, coatings, potting compounds, etc. Standard hardeners may be used		
Pot life (50 g) (hardening with PEPA) at 20 °C, min	25-40	25-40	25-40
Flash point, °C	About 155		
Refractive index (n_D)	1.529	1.535	1.540

Table 2. Low-viscosity Alkyl Resorcinol Epoxy Resins (improved quality)

Characteristics	AREM-2-28D	AREM-2-21E	AREM-2-20Q
Epoxy groups, %	27-30	19-22	19-22
Epoxide equivalent mass, g/mole	143-160	196-226	196-226
Epoxy value, eq/kg	6.3-7.0	4.4-5.1	4.4-5.1
Molecular mass distribution of diglycidyl ethers	$n=0$ 98 %	$n=0/n=1$ ~16/1	$n=0/n=1/n=2$ ~30/2/1
Average molecular mass	265-275	285-300	300-315
Modifier, %	<1	5-7	8-10
Volatiles, %	<0.1	<1.0	<1.5
Hydrolyzable chlorine, %	<0.1	<0.15	<0.2
Dynamic viscosity at 20 °C, Pa · s	0.2-0.6	1-3	1-3
Appearance	Light yellow liquid	Light yellow viscous liquid	Light brown viscous liquid
Degree of coloration (Gardner)	max. 5	max. 8	max. 8
Typical applications	Coating containing no volatile organic solvents, potting and encapsulating compounds etc.		
Refractive index (n_D)	1.5285	1.5312	1.5340

Table 3. High-purity Crystalline DGE of Alkyl Resorcinols

Characteristics	ARE-5MR	ARE-2,5DMR	ARE-5ER
Epoxy groups, %	36	34.5	34.5
Epoxyde equivalent mass, g/mole	118-120	124-125	124-125
Epoxy value, eq/kg	8.4	8.0	8.0
Molecular mass	$n=0$	$n=0$	$n=0$
distribution of diglycidyl ethers	99.9 %	99.9 %	99.9 %
Molecular mass	236	248	248
Volatiles, %	<0.1	<0.1	<0.1
Hydrolyzable chlorine, %	<0.01	<0.01	<0.01
Melting point, °C	66-72	102-105	40-44
Appearance	White crystalline powder		
Degree of coloration (Gardner)	max. 1	max. 1	max. 1
Type of initial phenol	5-methyl resorcinol	2,5-dimethyl resorcinol	5-ethyl resorcinol
Typical applications	Not stated		

Table 4. Solid Alkyl Resorcinol Epoxy Resins

Characteristics	ARE-1-4	ARE-2-8	ARE-5-13F
	Type of resin		
	Condensation product of 5-alkyl resorcinol epoxy resin with 5-alkyl resorcinols		"Phenoxy Resin" from 5-methyl resorcinol epoxy resin
Appearance	Brown solid mass	Reddish-brown solid mass	Colorless solid mass
Degree of coloration (Gardner)	15-16	min. 18	max. 1
Softening point, °C	85-95	75-80	65-75
Epoxy groups, %	2-5	5-8	12-14
Epoxyde equivalent mass, g/mole	830-2000	525-830	307-358
Epoxy value, eq/kg	0.05-0.12	0.12-0.19	0.28-0.33
Average molecular mass	1300-1800	760-880	760-830
Distribution of DGEs molecular mass	$n=5.3-7.8$	$n=2.6-3.2$	$n=2.8-3.3$
Hydroxyl groups, %	6.9-7.4	5.8-6.2	6.2-6.7
Volatiles, %	0.2-0.5	0.2-0.5	<0.05
Hydrolyzable chlorine, %	<0.6	<0.7	<0.01
Ash content, %	<0.2	<0.5	<0.1
Typical applications	As a component of cord adhesion promoters for the tire industry		For thermoplastic coatings and adhesives

Low-viscosity epoxy resins of higher quality, and crystalline diglycidyl oligomers, are characterized by the data presented in Tables 2 and 3. The first ones are unique products made from a mixture of low-molecular diglycidyl oligomers (over six articles) which show no tendency towards crystallization and remain liquid even after long-term storage. Crystalline resins are pure diglycidyl ethers made from only one alkyl resorcinol isomer.

Solid high molecular-weight alkyl resorcinol epoxy resins (see Table 4), are represented both by commercial technical products and pure "phenoxy resin" made from 5-methyl resorcinol and its diglycidyl ethers.

The possible routes for obtaining a wide range of typical AR epoxy resins (diglycidyl ethers) from low-viscosity liquids to solid compounds with epoxy group contents ranging from 3.6 to 36 % have been studied. These products, especially liquid resins, may be used as the main component in various special hardening compounds, as well as auxiliary chemicals (see Tables 1-4).

It is demonstrated that epoxy resins and pure diglycidyl ethers with special properties can be produced from shale-derived alkyl resorcinols as separated from water-soluble phenols. This is in addition to the possible production of common epoxy resins from these materials.

Acknowledgements

The author wishes to thank the Estonian Science Foundation for support under Grant No. 690.

REFERENCES

1. *Raidma E.* Diglycidyl ethers from shale oil alkyl resorcinols. Part 1. Initial raw phenols and the structure of reaction products // *Oil Shale*. 1994. V. 11. No. 3. P. 241-249.
2. *Raidma E.* Development of low-molecular epoxy resin production on basis of shale-derived alkyl resorcinols // *Liquid products of oil shale processing as raw for chemical industry: Sborn. nautshn. trudov NII slantsev*. Moscow, 1986. V. 24. P. 49-57 (in Russian).
3. *Sorokin V., Batog A.* The state and development perspective of epoxy resins manufacture technology // *Plast. massy*. 1984. No. 4. P. 36-39 (in Russian).
4. *Penczek P., Reidych J.* Development of investigations in the sphere of production of epoxy resins in the 80's // *Inf. bullet. po him. prom. SEV*. Moscow, 1987. No. 4. P. 19-28 (in Russian).
5. *Shode L. et al.* The basic trends of works by manufacture technology of low-molecular epoxy resins (review of literature) // *Lakokras. mater. i ih prim.* 1987. No. 4. P. 36-39 (in Russian).
6. *Sorokin M., Shode L., Elin O.* Development of investigations by formation of bisphenol-A type epoxy resins in two-stage additions of sodium hydrate // *Ibid.* 1988. No. 4. P. 7-9 (in Russian).

7. *Shode L. et. al.* Investigation of bisphenol-A type epoxy resin formation process in the presence of concentrated sodium hydrate solvents. The chemical conception of synthesis of bisphenol-A type epoxy resins in heterogeneous phase // *Ibid.* 1989. No. 3. P. 6-11 (in Russian).
8. *Lee H., Neville K.* Handbook of Epoxy Resins. New-York, San Francisco, Toronto, London, Sydney. McGraw-Hill Book Co. 1967.
9. Araldit-Harze und Härter für den Oberflächenschutz: Katalog CIBA-GEIGY. Basel (Schweiz), 1989.
10. *Steele S. M.* Epoxy resins as specialty chemicals // *Chemical Engineering Progress.* 1986. V. 82. No. 8. P. 33-35.

Presented by V. Yefimov

Received January 22, 1994