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### DIGLYCIDYL ETHERS FROM SHALE OIL ALKYL RESORCINOLS

#### PART 1. INITIAL RAW PHENOLS AND THE STRUCTURE OF REACTION PRODUCTS

##### 1. Water-soluble Oil Shale Phenols as Feedstock for the Synthesis of Epoxy Resins

Alkyl resorcinols (AR) and other phenolic compounds are formed by thermal processing of oil shale - kukersite. Water-soluble phenols accumulate in water layers of the retorting-unit condensation systems and additional quantities are obtained by washing the shale oil fractions with water. These phenol waters are subjected to dephenolization using a mixed extractant, particularly a mixture of butyl acetate and isopropyl ether. According to literature data [1, 4] the water-soluble alkyl phenols constitute up to 2 % of oil formed during oil shale retorting. From this amount, one-third is dissolved in the tar-water and two-thirds could be extracted from shale oil by supplementary washing. As is known from industrial practice of shale oil purification and phenolic water dephenolization, up to 8 kg of commercial water-soluble phenols (alkyl resorcinols) could be produced from one ton of shale oil.

Raw phenols of tar water represent a complex mixture (about 40 compounds) of alkyl derivatives both of oxybenzene (8-12 %) and resorcinol (88-92 %). The content of main alkyl resorcinols in the total phenols is as follows (data obtained between 1984 and 1988 at the Oil Shale Processing Association, which is now the state joint-stock company "Kiviter"): 5-methyl resorcinol (5-MR) -  $27 \pm 3$  %; 5-ethyl resorcinol (5-ER) -  $15 \pm 2$  %; 2,5-dimethyl resorcinol (2,5-DMR) -  $8 \pm 1$  %; and 4,5-dimethyl resorcinol (4,5-DMR) -  $8.5 \pm 1$  %. The main, and most suitable, method for obtaining alkyl resorcinol feed for the chemical industry is the rectification of raw phenols in a film-type rectifier, e.g. "Julius Montz" high-efficiency column. This type of equipment has been in use at "Kiviter" since 1982. The total yield of rectified fractions varies between 75-80 % of the initial amount of phenols, depending on the operating conditions.

The distilled fractions of shale phenols provide the raw material for manufacturing chemical products. Epoxy resins have already been produced from alkyl resorcinols for 20 years [3]. The possibilities for obtaining alkyl resorcinol fractions in the film-type column are based on the results of industrial balance tests of rectification (in 1986) and of laboratory investigations on vacuum rectification in a 3-5 litre still. The samples for gas-chromatographic analysis of distillate were taken at fixed yields during the entire batch rectification process [2, 5]. The results are illustrated by the typical dependences between the content of principal components in the distillate and distillation yield (Fig. 1). The maxima express the limit concentrations of the given component in the AR distillation fraction. Computer programs were written for

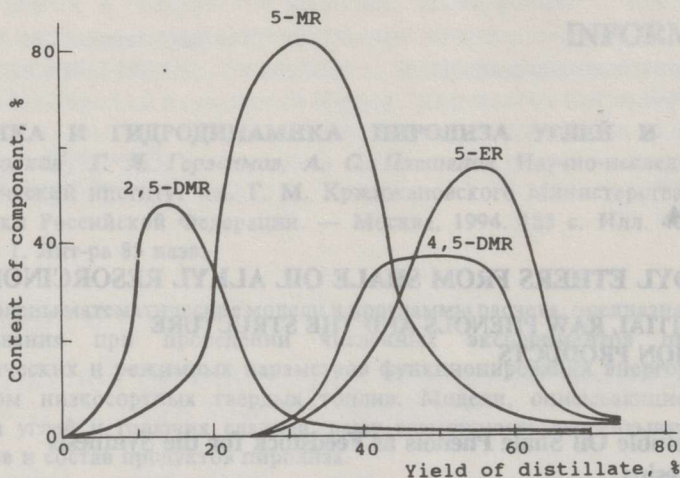


Fig. 1. Content of alkyl resorcinols in distillate plotted against the distillation yield

analyzing the data obtained in balance tests. These enabled an adaptive calculation of the content of individual components in virtually every fraction under study. The models of alkyl resorcinol fractions for industrial purposes were also evaluated [6].

Figure 2 shows the principal process for obtaining alkyl resorcinol concentrates for the synthesis of epoxy resins and pure diglycidyl oligomers. The fraction boiling between 295-320 (340) °C is the most suitable one for fundamental synthesis and industrial production of epoxy resins of the type AREM-2 a.o. from alkyl resorcinols. This fraction contains about 50 % of 5-AR and practically no (below 0.2 %) undesired component - 2,5-DMR. Diglycidyl ethers (DGE), from the mixture of 5-alkyl resorcinols, are low-viscous products and characterized by a low content of imperfect (defected) molecules. Special-purpose monomeric diglycidyl ethers are synthesized from AR crystal concentrates. The main characteristics of AR concentrates are presented in Table.

### Characteristics of Alkyl Resorcinol Concentrates Foreseen for the Synthesis of Epoxy Resins

Characteristic	Concentrate			Fraction 295-320 °C
	2,5-DMR	5-MR	5-ER	
Appearance	light crystalline powder with pinkish undertone			viscous yellow mass
Melting point	156	103	95	—
Average molecular mass	140	125	136	142
Content of hydroxyl groups, %	24.3	27.2	25.2	23.9

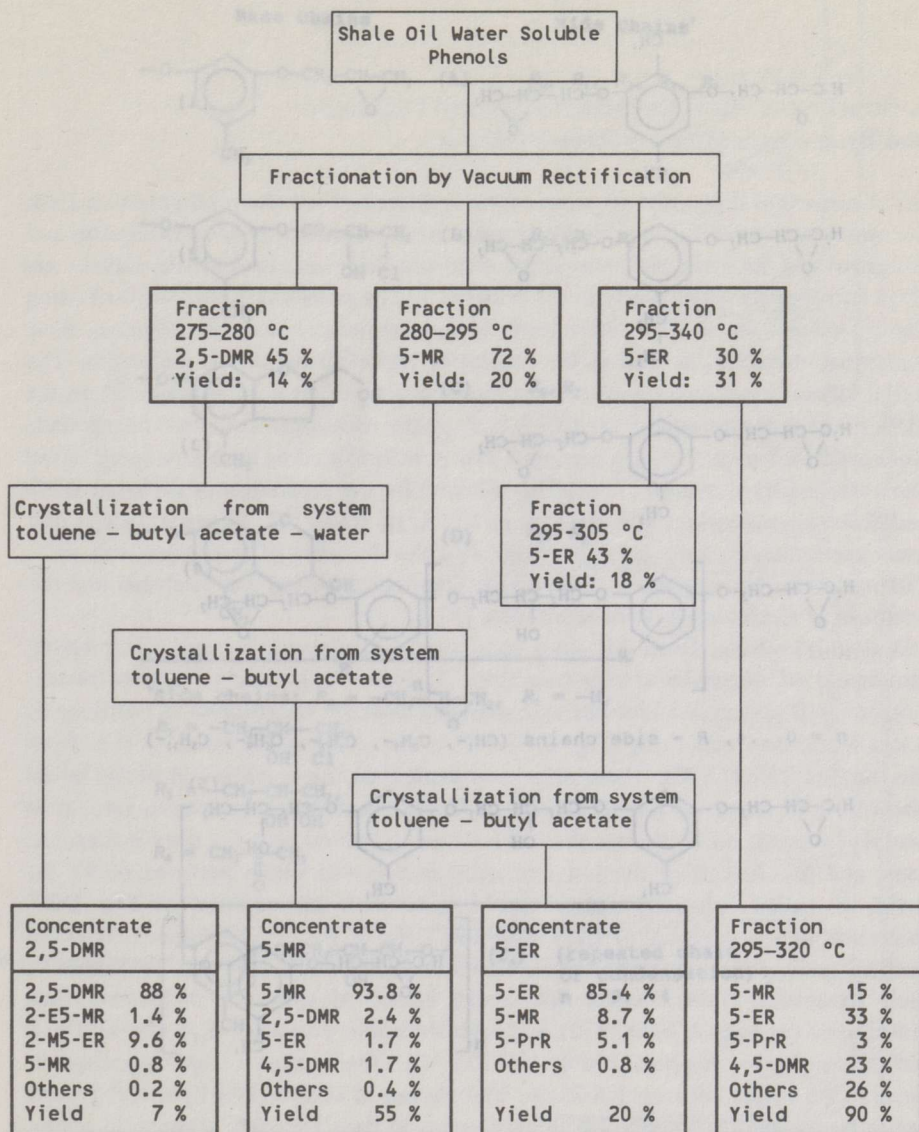
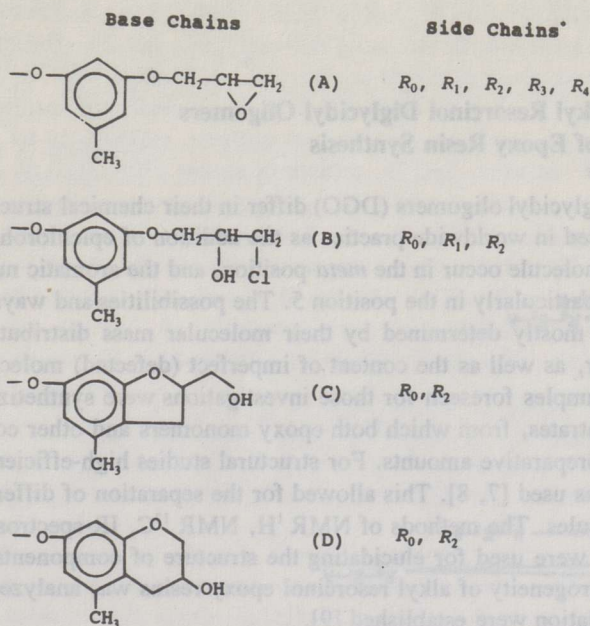


Fig. 2. Production of alkyl resorcinol concentrates for the synthesis of epoxy resins





\*Side chains:  $R_0 = -\text{CH}_2-\text{CH}-\text{CH}_2$ ,  $R_1 = -\text{H}$ ,

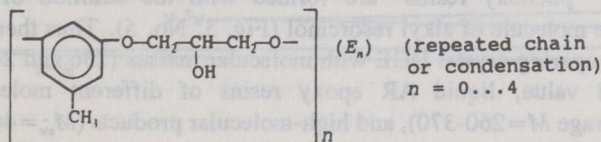
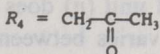
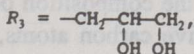
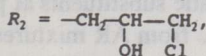


Fig. 4. Imperfect molecules of alkyl resorcinol epoxy resins (by-products)

AR concentrates, particularly distillation fractions, easily oxidize at elevated temperatures and in the presence of oxygen to form dark-coloured products. These are not suitable for the synthesis of epoxy resins which can meet present technical requirements.

## 2. Structure of Alkyl Resorcinol Diglycidyl Oligomers and By-products of Epoxy Resin Synthesis

Alkyl resorcinol diglycidyl oligomers (DGO) differ in their chemical structure from the epoxy resins used in worldwide practice as the addition of epichlorohydrin and the growth of the molecule occur in the *meta*-position, and the aromatic nucleus has alkyl substituents, particularly in the position 5. The possibilities and ways of using these products are mostly determined by their molecular mass distribution, their functional character, as well as the content of imperfect (defected) molecules. The initial laboratory samples foreseen for those investigations were synthesized on the basis of AR concentrates, from which both epoxy monomers and other compounds were separated in preparative amounts. For structural studies high-efficiency liquid chromatography was used [7, 8]. This allowed for the separation of different DGE and defected molecules. The methods of NMR  $^1\text{H}$ , NMR  $^{13}\text{C}$ , IR-spectroscopy and mass spectrometry were used for elucidating the structure of components as well. The molecular heterogeneity of alkyl resorcinol epoxy resins was analyzed and the products of C-alkylation were established [9].

Diglycidyl ethers, from AR pure concentrates, represent corresponding epoxy monomers of symmetrical structure (Fig. 3, Nos. 1, 2, and 3). Liquid resins, consisting of oligomer molecules with different aliphatic substituents at positions 5, 2 and 4 of the aromatic ring (Fig. 3, No. 4), are made from AR mixtures (i.e. from the fraction 295-320 °C). These structures depend on the composition of the initial phenols. The length of aliphatic chain is limited to five carbon atoms, i.e. up to pentyl. In liquid resins the number of repeated structural unit ( $n$ ) does not exceed four, and the content of the low-molecular part ( $n=0$ ) varies between 60-95 %. Solid, so-called "phenoxy resins" are formed with the addition of two DGE molecules to one molecule of alkyl resorcinol (Fig. 3, No. 5). Thus there exists the possibility for preparing crystal DGE with molecular masses (236 and 248) close to their theoretical value, liquid AR epoxy resins of different molecular mass distribution (average  $M=260-370$ ), and high-molecular products ( $M_{\text{av}}=460-2400$ ) of different softening temperatures ( $t=35-100$  °C). The content of epoxy groups in these resins varies between 3.6-36 %. The content of nonphenolic hydroxyl groups varies correspondingly from 7% in hard resins to their complete absence in epoxy monomers.

The quality of epoxy resins depends on the content of imperfect molecules in epoxy phenolic oligomers. These disturb the formation of durable three-dimensional polymeric materials (epoxy plastics) with a hardener. Physico-chemical functional characteristics of epoxy resins and their composition are presented by Pakter, et al. [8, 10, 11].



The functional defectiveness of epoxy oligomers is caused by the disruption reactions, incompleteness of the condensation processes (especially of dehydrochlorination), hydrolysis of chlorohydrines, reactions between epoxy and aliphatic secondary hydroxyl groups, etc. An epoxy resin synthesized from 5-methyl resorcinol and epichlorohydrin in alkaline media served as the main object of our investigations. The most specific structural elements (main and side chains), at whose combination the products of synthesis are formed, are given in Fig. 4. The epoxy resins from other AR, and their mixtures, form in an analogous manner. This is shown by the data of combined instrumental analysis, particularly by HPLC on "Dupon 8800" (UV-detector,  $\lambda=275$ , column of sorbax ODS 25x0.46 cm, eluent methanol-water). As a result, the following groups of compounds were identified:

- products of O-alkylation (DGE):  $R_0-A$ ,  $R_0-E_n-A$ ;
- by-products and hydrolysates of O-alkylation:  $R_1-A$ ,  $R_2-A$ ,  $R_3-A$ ,  $R_4-A$ ,  $R_1-E_n-A$ ,  $R_2-E_n-A$ ,  $R_0-B$ ,  $R_1-B$ ,  $R_2-B$ ,  $R_0-E_n-B$ ,  $R_2-E_n-B$ ;
- derivatives of dihydrobenzofuran:  $R_0-C$ ,  $R_2-C$ ,  $R_0-E_n-C$ ;
- derivatives of dihydrobenzopyran:  $R_0-D$ ,  $R_2-D$ ,  $R_0-E_n-D$ .

A typical chromatogram of epoxy resin prepared from 5-MR is given in Fig. 5. The content of hydrochloric compounds ( $R_2-A$ ,  $R_2-E_1-A$ ,  $R_2-E_2-A$ ) is elevated by addition of hydrochloric acid. As seen from the Figure, the desired product and imperfect molecules are separated according to both their molecular masses and functionality.

The retention time of a component depends directly on  $\log M$  (where  $M$  = molecular mass) which easily allows one to determine the homologous series according to their functionality. Only a slight dependence was established for the extinction coefficient as a function of the structure and the functionality of aliphatic fragments. This coefficient depends mainly on the substitution degree in aromatic ring [7]. For example, the contents of epoxy groups and oxidizable chlorine (as calculated from HPLC data and determined by chemical methods) differ by up to 10 %. This means that HPLC enables an effective control over the purity of epoxy resins synthesized from AR, and the determination of the content and nature of imperfect molecules. Besides the known structures in AR epoxy resins, the products of C-alkylation (derivatives of dihydrobenzofuran and dihydrobenzopyran) were detected. Their content may reach 40 % in the aforementioned epoxy resins (on an O-alkylation product basis). This depends upon the reaction conditions during the synthesis [9]. These compounds are not desirable for epoxy plastic preparation since they do not form three-dimensional structures in the reactions with amine hardener. Moreover, one can suppose that those oil-soluble products may also have an undesirable toxic effect on human skin.

Some of the imperfect molecules occurring in epoxy oligomers, and of some other unknown by-products, may act as colour carriers in synthesized products and also have a negative effect on the light resistance. The exact structure and action mechanism of those ingredients are not yet established.

Thus, the shale-derived alkyl resorcinols and diglycidyl oligomers (which are chemical compounds prepared considering their special characteristics) are of interest for additional detailed study and for their use in modern processes.



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