DEVELOPMENT OF ALKYLRESORCINOL-FORMALDEHYDE RESIN (DFK) CHEMISTRY AND APPLICATIONS

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*This review is dedicated to the memory of **professor AGU AARNA,** the founder and scientific supervisor of the Laboratory of Oil Shale Chemistry at the Tallinn Technical University. Development of the synthesis and application technology of adhesive resins from shale oil dihydric phenols is reviewed together with later studies concerning various resorcinol and 5-methylresorcinol poly- and co-polycondensates as well as their co-condensates with phenol and amides.*

The long-time scientific activity of professor Agu Aarna in the field of oil shale chemistry was outstanding and extensive. When he was asked, "What achievements have given you the greatest satisfaction," he often replied that adhesives from oil shale phenols or just: "DFK adhesives". This revelation might be taken as the main reason why this topic deserves greater attention and a more detailed treatment. Indeed, professor Aarna's scientific ideas proved to be most fruitful in this domain of shale oil chemistry, i. e., in the chemistry of resorcinolic resins which is one of the research topics at the Institute of Polymeric Materials of the Tallinn Technical University. Therefore, we do not confine ourselves to reviewing only the studies in which professor Aarna has been immediately involved, but survey this topic as it has been developed in the studies of his disciples up to the present day.

In 1957, a number of research laboratories were founded to promote research activities in the institutions of higher education. It is noteworthy that among the first 22 laboratories founded in the Soviet Union at that time, the Research Laboratory of Oil Shale Chemistry and Technology was founded in March 15, 1957 at the then Tallinn Polytechnical Institute. It has to be considered as an expression of great appreciation to the research supervised by professor Aarna. Professor Aarna held this position up to 1979. Naturally, the ties with the Laboratory were retained also during the following years.

Approaching the topic to be reviewed, we would like to stress one of the most basic standpoints inherent to professor Aarna's scientific heritage,

i. e., shale oil should be treated as a mixture of molecular complexes by considering all the physico-chemical phenomena involved [1]. In the oil, hydrogen-bonded complexes are formed between acidic and neutral oxygen-containing molecules, such as phenols and ketones. Phenols, separated from the water formed during the thermal processing of shale, were regarded as unpleasant waste. That belief was strengthened by unsuccessful experiments carried out in seeking for syntheses of useful products from them, the reaction with formaldehyde included [2]. Professor Aarna succeeded in entirely refuting that opinion. The first reference to successful synthesis of adhesives dates back to 1959, when professor Aarna wrote the paper "Adhesive Resin DFK" published in the Estonian journal "Technology and Production" [3]. This synthesis was successful due to considering the involvement of molecular complexes. The reaction of dihydric phenols, separated from the processing water, with formaldehyde was carried out in the presence of ketones (acetone). The name "DFK" was chosen to indicate that the reaction of dihydric phenols with formaldehyde was performed in the presence of a complexing agent.

At these times, the knowledge about the chemical composition of the mixture of dihydric phenols was poor and the high reactivity of these phenols as well as the degree of structuration of cured resins synthesised were not very well understood. The content of hydroxyl groups and reactivity referred to resorcinolic character, but based on the values of molecular weight it was concluded that the majority of these compounds should be dimethylresorcinols, of which 4,6-dimethylresorcinol was erroneously thought to be the most abundant one. Low functionality of

J. Vabaoja, K. Kiisler, P. Christjanson, A. Aarna and J. Tanner discussing the problems of DFK chemistry

these resorcinols led to the assumption that, in contrast to resorcinol, the methylol derivatives formed in the first step react further with phenolic hydroxyl groups with the formation of ethers [4, 5]. That assumption allowed a better explanation of the retarding effect of acetone, presumably due to the formation of H-bonds with phenolic hydroxyls. This erroneous assumption has later been corrected using new knowledge obtained about the composition of shale oil phenols.

Professor Aarna stood for a good balance between theoretical and applied studies which allowed to introduce the laboratory results relatively quickly into industrial application. The DFK adhesive resins are the best example of that practice. In co-operation with his disciple Karl Kiisler, a number of Soviet Union Author Certificates on the development of adhesive formulations and application technology were obtained [6]. Many of them were also patented in various countries. The first generation of industrially produced DFK-resins included three adhesives: DFK-1A; DFK-8 and DFK-9. Either a crude mixture of water-soluble phenols or a distilled alkylresorcinol fraction with the boiling range from 270 to 320 °C for DFK-1A, were used as raw material. The reaction with formaldehyde was carried out in the presence of acetone in all cases. Either sodium hydroxide was used as a catalyst (DFK-1A) or, as in the case of crude phenols, the reaction was performed in two steps with acid catalyst in the first step (sulphuric acid) and alkaline medium in the second step. These studies together with application technology formed the basics of Karl Kiisler's thesis [7].

To increase elasticity, the DFK-8 resin was modified with polyamide, which was dissolved in the mixture of phenols at 110 to 120 °C (~6 % of the resin) before the reaction. The DFK adhesives are two-component adhesives, i. e., depending on adherend materials and gluing technology, the proper amount of a suitable hardener-filler is added to complete the polycondensation reaction. A mixture of urotropin (hexamethylene-tetramine) and sawdust was used with the DFK-1A resin to manufacture highly water-resistant plywood by hot-pressing technology [8]. The mastic DFK-8, obtained by adding fillers (kaolin, lithopone) and a small amount of formalin, has been produced in large quantities for gluing polyvinylchloride floorings. With mainly gypsum-filled formalin-cured DFK-1A, good results have been obtained in gluing materials like asbestos-cement, foamed plastics and in bonding of silicate concrete construction elements [9].

Possibilities to use the DFK-9 resin for gluing various mineral construction materials were thoroughly studied in two theses supervised by professor Aarna and carried out by Ilja Auriste and Silvia Veiderma [10, 11]. The resin was cured with formalin, and silicalcite powder of specific properties was used as a filler. Much attention was paid to the physico-mechanical properties of adhesive bonds, especially to the causes of build-up of internal stresses and possibilities of their reduction with the use of special types of plasticisers (thiokols) in particular. The technology developed has been applied at a number of experimental buildings to glue silicalcite, in the production of large construction elements, and for gluing decorative dolomite plates to concrete walls.

A large step forward was made by professor Aarna's another disciple Ülo Lille, who thoroughly studied the chemical composition of shale oil phenols [12]. Gas-chromatographic analysis showed that the major component among water-soluble dihydric phenols is 5-methylresorcinol. The following step in the industry was fractionation of the mixture of crude phenols to obtain the 5-methylresorcinol fraction with the boiling range from 270 to 290 °C (Table 1). That fraction became the basic raw material for DFK resin synthesis. Rectification of the mixture leads to a significant increase of the share of 5-methylresorcinol and 2,5-dimethylresorcinol, and to reduction of the share of 5-ethylresorcinol and 4,5-dimethylresorcinol in the lower-boiling fraction. The content of the latter two components depends largely on the final temperature of rectification. The composition of phenols (Table 1) allows to characterise some peculiarities of that raw material as compared with the properties of pure resorcinol, which is widely used for polycondensation resin synthesis. As to electrophilic aromatic substitution, alkylresorcinols:

- are of higher reactivity because of the high content of *meta*-alkylated resorcinol derivatives with 5-methylresorcinol being the major one. Most of the dialkylderivatives are also 5-alkylated;

- consist of compounds of different reactivities varying from the most reactive 5-methylresorcinol to trisubstituted resorcinols, e. g. 2,4,5-trimethylresorcinol;

- contain components of different functionality with overall functionality being lower than that of resorcinol mainly because of the presence of 2,5- and 4,5-dimethylresorcinols.

Table 1. **Characteristics of Shale Oil Water-Soluble Phenols**

Characteristic	Crude phenols	Fraction 270-290 °C
Average molecular weight	140-150	125-135
Hydroxyl content, %	20.4-22.1	23.8-24.8
Monohydric phenols, less than	10	2
5-Methylresorcinol	26-32	50-60
5-Ethylresorcinol	10-15	2-8
2,5-Dimethylresorcinol	6-10	12-18
4,5-Dimethylresorcinol	7-10	4-8
Total of these four resorcinols	50-60	75-80
Trifunctional resorcinols	40-50	55-65
Average of reactive sites per molecule	Not determined	2.6-2.7

By that time, professor Aarna's ideas about utilisation of shale-oil water-soluble phenols as a raw material for chemical industry became more and more important because it was understood that the resorcinolic resins are indispensable in many areas of application where curing at ambient temperature and high resistance to atmospheric conditions are of great importance. High price of the synthetic resorcinol limits a still wider use of resorcinol resins. In that sense the Estonian oil shale is a unique source of alkylresorcinols, which are obtained as a by-product in thermal

processing. Good perspectives for usage of these alkylresorcinols induced extensive changes in the research areas of the Laboratory of Oil Shale Technology. Alkylresorcinol resins as a part of resorcinol resin chemistry and their application together with proper technology became the main research topic of the Laboratory.

Estimation of the reactivity of various resorcinol derivatives in the mixture of shale oil alkylresorcinols with respect of formaldehyde in aqueous solution (polyoxymethyleneglycols) is a complicated task. Assuming that the logarithm of the first-order rate constant with respect to formaldehyde depends linearly on the initial water content, the following estimation for the reactivity was obtained [13]:

Resorcinol	1
Mixture of alkylresorcinols	4.3
5-Methylresorcinol	95.5

We have found that the rate of hydroxymethylation of the alkylresorcinol mixture exceeds that of resorcinol by 4 to 6 times. Considering the 50-60 % content of 5-methylresorcinol, it is clear that the presence of other alkylresorcinols in the mixture must considerably decrease the rate of the reaction of 5-methylresorcinol. The degree of conversion of 5-methylresorcinol only slightly surpasses that of 5-ethylresorcinol, but considering the higher content of 5-methylresorcinol, the properties of the resins are mainly determined by the oligomers of 5-methylresorcinol, which predominate in the product mixture. 4,5-Dimethylresorcinol and other still less reactive resorcinols mainly take part in the polycondensation reactions, characterised by a low degree of conversion under the conditions of formaldehyde deficiency. The presence of alkylresorcinols of widely different reactivity leads to non-homogeneity of the chemical structure of oligomers which can not be considered to be an advantage of alkyl-resorcinol resins.

In the search for effective complexing agents, caprolactam has been found to be a suitable additive. Molecular complexes of phenols (resorcinols included) with caprolactam have been studied using melting diagrams and infrared spectrometry [14, 15]. The rate retarding effect of caprolactam on the reaction of alkylresorcinols with formaldehyde appeared to be much stronger than that of acetone [16]. The effect is particularly strong in the polycondenation of the initially formed methylolresorcinols. The strength of H-bonds between the phenolic hydroxyl and the carbonyl of caprolactam is enhanced by the conjugation effect in the amide group. The formation of H-bonds changes the electron distribution at the phenolic ring and hence, the reactivity of active *ortho-* and *para-*sites. It is also obvious that the dominating trifunctional phenols allow highly structured polycondensates to be formed without involvement of phenolic hydroxyls.

Based on these results, a new adhesive resin containing caprolactam (DFK-4) has been developed and introduced into industrial production [17]. That resin has been used to glue foamed plastics to metallic surfaces in shipbuilding. It has been better than other DFK resins also in gluing various mineral materials (asbestos cement, dolomite). These problems

have been the topic of the thesis of Peep Christjanson (supervised by professor Aarna) [18]. The DFK-4 had many advantageous properties in comparison with earlier DFK brands. First, it must be noted that water could be easily separated by vacuum distillation after synthesis. The application areas of an aqueous-free resin were much wider and also, the physico-mechanical properties of the adhesive bonds were better. The rate-retarding effect of caprolactam is stronger than that of acetone, which shows also in the longer working-life of the adhesive.

Good results with molecular complexes of phenols with caprolactam awoke interest toward other amides as complex-formers. Professor Aarna's next postgraduate student Jüri Vabaoja identified a number of crystalline complexes of phenols (also resorcinols) with imides, substituted amides and urea using melting diagrams and IP spectrometry as analytical tools [19, 20]. Jüri Tanner in his thesis work (under supervision of professor Aarna) used dielectric constant measurements and cryoscopy to study molecular complexes of amides (lactams incl.) with phenols [21]. Although these studies had substantially improved the knowledge about molecular complexes between phenols and amides, caprolactam remained to be the best rate-retarding agent in the composition of adhesive resins.

For better understanding of the kinetic properties of polycondensation reaction of resorcinols in multicomponent concentrated systems containing coplexing agents, more profound studies were required. The generally first order reaction with respect to formaldehyde allowed to quantitatively estimate the behaviour of different resorcinols and complexing agents. In the first study [22] of the series, it was found that the presence of caprolactam (1-2 moles) retards the rate of 5-methylresorcinol reaction with formaldehyde by about 5-6 times at 30-40 °C in comparison with the reaction in aqueous solution of the same concentration.

In case of the mixture of alkylresorcinols, the reaction proceeds in two steps. The relative amount of formaldehyde reacted in both steps depends on the amount of caprolactam taken. With larger caprolactam amounts, the formation of methylolcaprolactam cannot be excluded. It is quite obvious that the formation of molecular complexes of phenols with amides decreases the relative reactivity of phenols and enhances that of amides because of amide group conjugation. If amides of higher reactivity are used, the reaction rate is increased in the system resorcinol/urea, where amide appears to be the preferred reacting component [23]. To characterise the hydroxymethylation reaction of the systems consisting mainly of phenols and amides, an empirical relationship has been derived by Karl Kiisler et al.:

$$k_{ef} = k \, n \, m,$$

where: k_{ef} - experimental rate constant;

k - rate constant characteristic of the system;

$n = n_0 - K_a$ and $m = m_0 - K_a'$ are active molar ratios, where

n_0, m_0 are the initial molar ratios of components, and K_a and K_a' are constants which can be found from the linear relationships:

$k_{ef} = f(n_0)$ and $k_{ef} = f(m_0)$ if at different m_0 and n_0 values the $k_{ef} = 0$.

In case of four-component system, the third active molar ratio is added into the relationship. The characteristic rate constant for a system can be used as a quantity characterising the reactivity and the effect of H-bonds. The kinetics of hydroxymethylation reaction of resorcinols and lactams has been studied in the thesis work of Kadri Siimer (supervised by professor Aarna) [25].

Table 2. **Kinetic Parameters of Hydroxymethylation Reaction for Aqueous Solutions at 60 °C**

Substrate	Complexing agent	Characteristic rate constant k, h^{-1}	Relative k
Resorcinol	-	0.68	1
5-Methylresorcinol	-	71.1	104
Caprolactam	-	0.073	0.11
Pyrrolidone	-	0.12	0.18
Resorcinol	Caprolactam	0.096	0.14
5-Methylresorcinol	Caprolactam	5.25	7.7
Caprolactam	Phenol	0.25	0.37

As can be seen from Table 2, the reaction rate of different resorcinols decreases in the presence of lactams with the additional effect of levelling of the relative reactivities. In the system caprolactam/phenol, the reacting component is caprolactam, whose relative reactivity is enhanced by the formation of H-bonds as discussed earlier.

Although the formation of molecular complexes has been successfully used to control the reactivity of alkylresorcinols, both in laboratory and in industrial applications, that method cannot be considered to be the most effective one. Greater control over the reactivities of resorcinols can be achieved under conditions where the reactivity of resorcinols is of secondary importance, and the reactant would be the rate-determining component. These conditions are met to some extent in the systems where resorcinol is reacted with hydroxymethyl derivatives (methylol compounds). Among these compounds, our main interest have been methylolcaprolactam, di-, and monomethylol ureas and also various methylolphenols. The main aim has been to find optimum conditions for the formation of copolycondensates with maximum yield. Due to substantial levelling of the relative reactivities and decrease of the overall reaction rate, a more balanced conversion of different resorcinols has been observed under such conditions. So, by incorporating various condensing reagents into the resin structure it has been possible to more effectively use the highly reactive resorcinols of the alkylresorcinol mixture. A retarded reactivity of the co-polycondensation prepolymers toward a hardener makes their use technologically more convenient.

Practical realisation of the reaction of methylol compounds with alkylresorcinols gave a number of new DFK resin formulations and modified technologies for their usage. Polycondensation with methylolcaprolactam gave the adhesive resin DFK-11 [26], which has been successfully used in gluing various polymeric materials. Inclusion of monofunctional caprolactam into the resin structure leads to resins of

lower degree of structuration and higher elasticity. Variation of the reaction conditions and the partial use of formaldehyde allows to synthesise co-polycondensates of expected ratio of alkylresorcinols and caprolactam.

Mixing of the aqueous-ethanol solutions of alkylresorcinols and dimethylolurea gave the DFK-12 for wood impregnation [27]. This technology has been used to manufacture skis with edges made of impregnated wood, which increases the wearing resistance. It has to be noted that the technology has been very convenient as polycondensation of monomers in the impregnated wood takes mainly place in one cycle during the gluing operation at temperatures from 100 to 120 °C. Later, the technology has been modified so that hexamethylenetetramine was used instead of formaldehyde in the preparation of the impregnating mixture DFK-20 [28].

It can be assumed that the main application area of alkylresorcinol adhesives is wood gluing as it is the case with resorcinol adhesives. The only accepted adhesives for gluing weatherproof wooden constructions are the resorcinol- or phenol-resorcinol adhesives. Good adhesive properties are obtained with the alkylresorcinol adhesive DFK-1A of increased alkali content (DFK-1AM). However, that resin is technologically inconvenient to use for gluing large constructions because of a too short working life.

By co-polycondensation of methylolphenols with alkylresorcinol mixture, the synthesis and technology of the phenol-alkylresorcinol resin DFK-14 was developed [29]. This resin is characterised by a relatively low free phenol content (~3 %) as compared with standard phenol-resorcinol resins, and working life of the DFK-14 can be controlled by the amount of an alkaline catalyst. A mixture of paraformaldehyde and wood flour is used as a hardener with that resin. The physico-mechanical properties of adhesive bonds and resistance to atmospheric conditions are comparable to those obtained with standard phenol-resorcinol resins. The DFK-14 has been successfully used in manufacturing adhesively bonded wooden constructions. The study of the reaction of methylolphenols with alkylresorcinols and urea allowed to develop the production technology of the binder DFK-16 used in the manufacturing of mineral-wool insulation materials [30]. Basics of the synthesis of alkylresorcinol-formaldehyde resins and areas of their application have been reviewed in several papers [31-35].

Study of the hydroxymethylation-polycondensation reaction has been a complicated task because of analytical difficulties in the determination of formaldehyde distribution between the numerous compounds present at different stages of the reaction. Important characteristics of the chemical composition of the resins is the content of methylene links in different chemical environments - the isomeric composition. ^{13}C and ^{1}H NMR spectrometric methods have proved to be the most powerful tools in the resin analysis so far. These methods have given reliable information about the isomeric composition of various phenolic resins. Quantitative determination of the content of various structural fragments based on integral intensities of various ^{13}C and ^{1}H signals has been successful in

Table 3. Molecular-Weight Distribution and Isomeric Composition of Some Polycondensates

Parameter, content, %	R/F = 1/0.5	5MR/F = 1/0.5	R/F = 1/0.5; NaOH - 0.08	5MR/F = 1/0.5; NaOH - 0.08	R/F/C* = 1/0.5/0.5	5MR/F/C = 1/0.5/0.5	R/5MR/F = 1/1/1	R/5MR/F/C = 1/1/1/1
Unreacted R, 5MR*	32	21	39	31	29	26	13 (20 + 3)	25 (22 + 3)
Dimers	15	25	6	10	15	22	17	17
Trimers	12	20	6	10	11	19	15	12
Tetramers	13	11	-	-	9	13	15	12
Higher oligomers	28	23	49	49	36	20	30	40
-CH$_2$-:								
4,4'	82	71	87	66	-	-	76; 60	74; 62
2,4'	17	27	13	34	-	-	24; 40	26; 38
F in co-oligomers	-	-	-	-	-	-	57 (55)*	-
Mole ratio 5MR/R in copolycondensate	-	-	-	-	-	-	1.6 (1.6)**	1.8

* R - resorcinol; 5MR - 5-methylresorcinol; F - formaldehyde; C - caprolactam.
** In ethylene glycol.

most cases. ^{1}H NMR has proved to be most useful in following the course of the reactions used in resin synthesis.

The more informative ^{13}C NMR spectrometry has been used in determination of the isomeric composition of various resins and in determination of the chemical structure of oligomers separated by preparative liquid chromatography, which also gives the molecular-weight distribution of resins [36-40]. Resorcinol and 5-methylresorcinol having the largest difference in reactivities with respect to formaldehyde considering the composition of alkylresorcinol mixture, have been used in studying the polycondensation reaction in greater detail. 5-Methylresorcinol has been chosen as the model compound also because of being the most abundant component in the mixture of shale oil alkylresorcinols. Results of the determination of the chemical composition of some polycondensate prepolymers synthesised under identical conditions are presented in Table 3 [41, 42]. The study of the influence of various catalysts on the resin structure showed that alkaline and acidic catalysts lead to rise in the degree of polycondensation and enhanced 2-substitution in case of 5-methylresorcinol [37, 43, 44].

From various polycondensation experiments with resorcinol and 5-methylresorcinol, the following conclusions can be drawn:

• Chemical structure and isomeric composition of polycondensates are mainly determined by the nature of the phenolic component.

• 5-Methyl substituent leads to a substantial increase of the substitution at C2 between the two hydroxyl-bearing carbons, thus diminishing the regularity of the chemical structure of polycondensates.

• The degree of conversion of 5-methylresorcinol is always higher regardless of experimental conditions used.

• 5-methylresorcinol gives polycondensates of a more uniform molecular-weight distribution reflected in a higher content of dimeric and trimeric oligomers. This is apparently a favourable feature of 5-methylresorcinol polycondensates.

• The structural differences of resorcinol and 5-methylresorcinol polycondensates in the presence of caprolactam are of minor importance compared to the rate-retarding effect. Ethylene glycol has a slight levelling effect in case of co-condensation of these two phenols.

• Various catalysts lead generally to a higher degree of polycondensation, broadening of the molecular-weight distribution of polycondensates and in case of 5-methylresorcinol, also to enhanced 2-substitution.

The chemical structure of resorcinol and 5-methylresorcinol co-polycondensates is not affected by the presence of levelling agents like caprolactam or ethylene glycol to any significant extent. Due to the differences in reactivity, monomeric resorcinol (85 %) prevails among the unreacted monomers. The more reactive 5-methylresorcinol predominates in the structure of oligomers. At the same time, the amount of formaldehyde bound into co-oligomers is fairly high reaching 55 to 57 %. Resorcinol is predominantly included into the structure of co-oligomers at the ends. This refers to the reaction of the relatively less reactive resorcinol mainly in the stage of condensation.

Stepwise reaction is used in the synthesis of phenol-resorcinol- and phenol-alkylresorcinol-formaldehyde resins. An alkaline mixture of methylolphenols and low-molecular-weight phenolic oligomers is synthesised in the first step. This mixture is further condensed with the resorcinolic component. Thin-layer chromatographic analysis allowed to estimate that the reaction rates of resorcinol and 5-methylresorcinol with methylolphenols are rather similar. The reaction of free phenol in the mixture is negligible [45]. The formation of phenolic resin due to the homocondensation of methylolphenols along with the co-condensation reaction is also of minor importance. In the polycondensation of methylolphenols with the mixture of resorcinol and 5-methylresorcinol, the difference in their relative reactivities still determines the degree of their conversion despite the substantial levelling of reactivities. For example, in the reaction with *ortho*- or *para*-methylolphenol, a 1.7/1 or 3/1 ratio of unreacted resorcinol/5-methylresorcinol has been obtained [46, 47]. The same ratio for the 1/1/1/ reactant ratio in case of free formaldehyde in aqueous solution equals to 6.7 (Table 3).

Table 4. **Characteristics of Polycondensates**

Property	P/F = 1/1.5	P/F/R = 1/1.5/1.2	P/F/5MR = = 1/1.5/1.2
	NaOH 0.14 moles		
Unreacted phenol (P), %	11	3	5
Unreacted resorcinol (R) or 5-methylrecorcinol (5MR), %	-	23	26
Amount of polycondensate, %	-	74	69
Formaldehyde (F) distribution, %:			
p-CH$_2$OH	22	2	2
o-CH$_2$OH	64	18	20
-CH$_2$-:			
p,p'-	10	12	13
o,p'-	4	12	8
o,o'-	-	9	3
4,*p*-	-	16	15
4,*o*-	-	31	34
2,*o*-	-	-	5
Co-condensate total, %	-	47	54

Characteristics of some co-polycondensates synthesised from resorcinol and 5-methylresorcinol under the conditions of industrial synthesis are presented in Table 4 [46]. Polyfunctionality of phenolic components leads to the formation of a large number of isomeric oligomers. At that, the chemical structure of phenol/resorcinol and phenol/5-methylresorcinol resins is rather similar except for the higher degree of 2-substitution in 5-methylresorcinol resins in the prepolymer state. In both cases, nearly 50 % of formaldehyde is bound in co-oligomers. The reactivity of methylol compounds is the rate- and conversion-determining factor in the co-condensation reaction. High reactivity of resorcinols with respect to

Table 5. Co-Condensation Rate Constants of *ortho*- or *para*-Methylolphenol with Resorcinol and 5-Methylresorcinol

Molar ratio cat. HMP*	Rate constant, min^{-1} × 10^3						$k_{p\text{-HMP}}/k_{o\text{-HMP}}$		R-CH$_2$- in the mixture of R/5MR	
	o-HMP/R = 1/1	o-HMP/5MR = 1/1	o-HMP/R/5MR = 1/1/1	p-HMP/R = 1/1	p-HMP/5MR = 1/1	p-HMP/R/5MR = 1/1/1	R	5MR	o-HMP	p-HMP
					Catalyst: n o n e					
-	27.2	25.2	31.5	66.0	43.3	45.6	2.43	1.72	24-28	18-20
					Catalyst: NaOH					
0.025	27.3	24.7	-	132.6	77.9	-	4.85	3.16	-	-
0.05	25.7	25.0	-	161.2	111.8	141.5	6.27	4.47	-	24-28
0.1	30.5	25.2	34.7	210.1	182.4	-	6.88	7.24	35-40	-
					Catalyst: Zn(OCOCH$_3$)$_2$					
0.005	60.3	40.8	-	147.5	71.1	-	2.45	1.74	-	-
0.01	103.5	53.3	-	261.6	90.0	123.8	2.53	1.69	-	26-29
0.015	113.6	73.7	121.6	-	133.3	-	-	1.81	26-29	-
					Catalyst: C$_6$H$_5$COOH					
0.025	59.8	45.3	-	247.6	138.6	147.5	4.14	3.06	-	34-36
0.05	99.0	69.3	95.0	-	203.9	-	-	2.94	32 - 36	-

* *o*-HMP - *ortho*-hydroxymethylphenol; *p*-HMP - *para*-hydroxymethylphenol; R - resorcinol; 5MR - 5-methylresorcinol.

electrophilic substitution is only of secondary importance. At that, the first among methylolphenols to react is the *para*-derivative.

The rate constants of co-condensation of some individual hydroxy-methylphenols with resorcinol and 5-methylresorcinol in the melt at 120 °C in the presence of various catalysts were determined using ^{1}H NMR spectrometry.

It appeared that resorcinolic rings are preferably substituted at the two equal positions. Only with alkaline catalyst and only in case of *ortho*-methylol derivative, multiple substitution is promoted. Study of the co-condensation kinetics of *o*-methylol-2,4-xylenol and *p*-methylol-2,6-xylenol with resorcinols has shown higher reactivity of the first in case of non-catalysed and zinc acetate-catalysed reactions [48, 49]. Both alkaline and acid catalysts promote preferably the reaction of *para*-derivative. The complicated total effect of *ortho-para*-directing substituents eventually results in low reactivity of the *para*-methylol groups. The homo-condensation of the xylenols mentioned excludes the possibility of a direct reaction [50]. The reaction pattern includes the formation of intermediate ethers. It has been found that alkali is the most effective catalyst for *p,p*-dimethylene ether formation and for the cleavage of formaldehyde from them. Ethers from *ortho*-derivative and also from dimethylol-*p*-cresol are exceptionally stable as to formaldehyde release, and they are more liable to decompose with the release of free phenol.

Technologically it is more important to study the co-condensation of resorcinol and 5-methylresorcinol with *ortho*- and *para*-methylol phenols, which are the first-formed and most abundant components in the mixture of methylolphenols synthesised in the first step co-polycondensation. Some of the results obtained are presented in Table 5 [51, 52]. Direct reaction has been the only reaction observed under the conditions used. There has been no evidence of parallel homo-condensation of methylolphenols or cleavage of free formaldehyde. Ratios of the apparent rate constants quite clearly indicate the higher reactivity of *para*-methylol derivatives in all cases studied. The rate difference obviously results from a higher stability of the *para*-quinoidal form of the methylol-derivative on one hand, and from a strong rate-retarding effect of the intramolecular H-bond in *ortho*-derivatives on the other. Both alkaline and acid catalysts enhance preferably the reactivity of *p*-methylolphenol.

The most effective catalyst is zinc acetate enhancing the co-condensation rate of two methylols equally. This can be explained by the like influence of intramolecular H-bond and zinc-co-ordination bond in case of *ortho*-derivative as compared to the effect of respective intermolecular bonds on *para*-derivative. Co-condensation rate of resorcinol is larger compared to that of 5-methylresorcinol, especially in case of co-condensation with *para*-methylol derivative. It allows to predict that the co-condensation of resorcinol is preferred if the mixture of both resorcinols is used.

However, the actual distribution of methylene linkages (Table 5) between the oligomers clearly shows that the reaction of 5-methyl-resorcinol is preferred. Both alkaline and acid catalysts increase the amount of resorcinol-linked methylenes. We can only conclude that in the

concentrated systems, simultaneous operation of the complex physico-chemical effects leads to substantial changes in relative reactivities of substrates when reacting them in the mixture. The co-condensation studies have revealed the necessity to study the homo-condensation reactions of *ortho-* and *para*-methylolphenols in greater detail [51, 53]. It appeared that homo-condensation of the *para*-derivative is preferred in all combinations studied. Homo-condensation proceeds over the intermediate dimethylene ether formation as a rule, except in case of an alkaline catalyst. At the following step, phenolysis of ethers occurs rather than formaldehyde release, leading to the domination of *o,p*-methylene isomers among the products. In addition, the rearrangement of *p*-methylol groups into *ortho*-positions takes place.

Table 6. **Share of the Amidomethylation Reaction**

Molar ratio of N-methylolcaprolactam/resorcinol	Share of amidomethylation		
	Resorcinol	5-Methyl-resorcinol	Alkyl-resorcinols
0.25	100	80	52
0.5	74-100	76-80	54
0.75	67	72	55
1	60-70	65-70	54

With methylolamides as condensing agents, co-condensation is not favoured under alkaline conditions. The rate of homo-condensation is limited by a slow decomposition of methylol compounds. This phenomenon explains why the reaction rate is independent of the type of resorcinol taken to study the reaction [54]. Under neutral conditions, the amidomethylation of resorcinols takes place with the formation of mainly asymmetrical methylene derivatives (Table 6). It can be expected that in case of the mixture of alkylresorcinols, higher degree of alkylation might decrease the extent of amidomethylation of those derivatives [55]. Among the products, mono-amidomethylated resorcinols prevail. The share of 2-substituted resorcinols varies from 20 to 28 % [56]. In co-condensation of the equimolar mixture of resorcinol and 5-methylresorcinol with methylolcaprolactam (1/1/1), the ratio of unreacted resorcinol/5-methylresorcinol is 1.3 to 1 [57]. It means that methylolcaprolactam is substantially more effective than methylolphenols in levelling the relative reactivities of resorcinol and 5-methylresorcinol.

In the presence of acid catalyst, amidomethylation is the only reaction to occur [55, 58]. The first step of the reaction involves the formation of an equilibrium amount of the dimethylene ether of caprolactam [59]. Both methylolcaprolactam and the ether are capable to provide the carbonium ion required for the electrophilic attack to take place at the phenolic substrate. Amidomethylation has also been successful with 2,5-dimethylresorcinol and the mixture of shale oil alkylresorcinols as substrates [55]. Depending on the molar ratio of components, the mixture of mono-, di- or trisubstituted compounds with methylolamide are formed. ^1H and ^{13}C NMR spectrometry have been used to follow the course of the

reaction or to determine the distribution of the caprolactam-linked methylenes of 2- and 4-mono, 2,4- and 4,6- di- and 2,4,6-trisubstituted resorcinol and 5-methylresorcinol and the shares of amidomethyl groups bound with the phenolic component during the amidomethylation reaction, in the final product mixtures as well as in the chromatographically separated fractions [41, 56, 60]. With mono-functional methylolcaprolactam it has been possible to study the acid-catalysed electrophilic substitution in monohydric phenols without the interference of further condensation [61]. Because of a lower relative reactivity of phenol, also methylenedicaprolactam has been found besides the products of amidomethylation.

The reaction of methylolphenols with caprolactam and methylolcaprolactam has also given interesting information about the co-condensation pattern [62]. The reaction of two different methylolphenols in the presence of acid catalyst (HCl) gives preferably asymmetrical dimethylene ethers. Ethers from *ortho*-methylols do not release formaldehyde. The following heating at 130-150 °C gives N,N'-methylenedicaprolactam and the free phenol. The dimethylene ether from *para*-methylolphenol decomposes already at 80 °C with the formation of symmetrical ethers with subsequent formaldehyde release. The reaction of *o*-methylolphenol with caprolactam follows the mechanism of amidolysis of the preliminarily formed phenolic dimethylene ethers to give the same asymmetrical methylene derivatives, which are more convenient to prepare by the reaction of phenols with methylolcaprolactam.

A thorough study of isomeric composition and the chemical structure of various resorcinol and 5-methylresorcinol poly- and co-polycondensates with formaldehyde, methylolphenols and methylolcaprolactam (30) in the prepolymer as well as some of them in the cured state has been summarised in Helle Lippmaa's thesis [63]. This dissertation work remained the last one in the series of the studies in the field of resorcinolic resins supervised by professor A. Aarna. The research methods used here included the combined liquid chromatography/^{13}C NMR in liquid and CP MAS ^{13}C NMR in the solid state. The chemical structure of 57 compounds with assignment of all ^{13}C chemical shifts have been identified.

The structural properties of the cured resins are generally similar to those of prepolymers except, of course, a higher 2-substitution and branching after the reaction with additional formaldehyde (from 0.5 moles in prepolymer to 1.2 moles for curing). The differences in the structure of cured resins depend mainly on the conditions of the curing reaction. The structure and also the physical properties obtained in the presence of water differ from those obtained in the melt [43, 64, 65]. The presence of water (in case of curing with formalin) facilitates a more even distribution of the reagent and the structure is more regular in substitution pattern than that in the case of curing with paraformaldehyde in the melt. It is also interesting to note that in physically completely cured resins, both resorcinolic as well as the phenol-formaldehyde resins, the chemical reactions have not necessarily reached exhaustion of the reagents. Spectra taken after long time storage of resin samples containing paraformaldehyde

residues (resorcinolic) or methylol groups (phenolic) show the continuance of the reactions in the solid phase.

In further studies, attempts have been made to include urea into the structure of resorcinolic resins. This would allow to substantially increase the durability and weather-resistance of urea resins. The reactions of resorcinols with methylolureas follow the same pattern as observed with of other methylol compounds studied. Because of high reactivity, methylolureas are formed right in the reaction mixtures containing resorcinols thus simplifying the technology of synthesis. However, highly selective conditions are required to ensure the preferential formation of co-condensates instead of only urea homo-oligomers. A large excess of resorcinol has to be used to obtain co-polycondensates through the reaction with mono- and dimethylolureas in aqueous solution at 60 °C, with weak acid catalyst promoting the co-condensation [66]. Amide homo-condensates are easily formed in the reaction mixture because the difference in the relative reactivities favours the reaction of urea with formaldehyde. Besides, the nature of equilibrium attained in the reaction system provides better possibilities for resorcinol homo-condensation with the formaldehyde released from labile urea intermediates. The formation of co-cndensates is favoured in the reactions either of methylolphenols with urea or phenols with methylolureas in the presence of acetic acid catalyst [67]. The amidolysis of the first-formed dimethylene ethers of phenols or the phenolysis of dimethylene ethers of urea are the key reactions to be considered.

We hope that this short review can be regarded as a small contribution to the chemistry and application of polycondensation resins of resorcinol and shale oil alkylresorcinols made possible by professor Agu Aarna's initiative. It has to be noted that a great many ideas for the studies


Application of DFK resins in the production of skis (in the bottom corner - the trade mark of DFK)

described have been initiated by him. Professor Aarna never denied to share his bright ideas with colleagues, and has been a great teacher and an inspiring lecturer for us as his students and disciples.

The references presented include a number of studies published and applied in Japan. That is because since 1979, the DFK-alkylresorcinol resins have been produced by the Japanese company "Nagoya Oilchemical" with oil shale alkylresorcinols being the raw material, purchased from the Estonian oil shale industry.
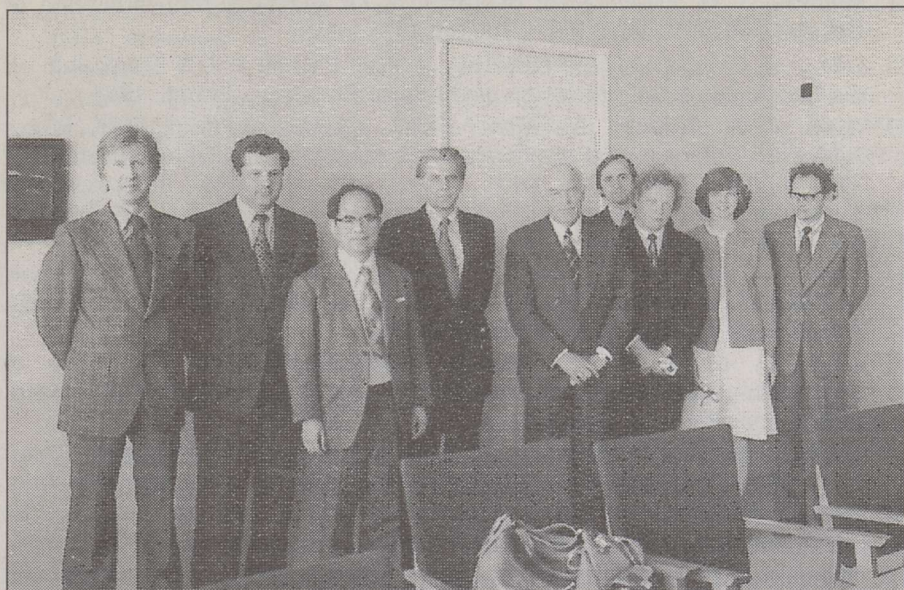
President of the "Nagoya Oilchemical" Mr. S. Horiki (3rd from the left) visiting the laboratory

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