METHODS OF ASSESSING FUEL AND OIL QUALITY

COMPOSITION OF PRODUCTS FROM ALKYLATING DIPHENYLAMINE WITH OLEFINS ON ALUMINUM CHLORIDE

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An investigation of antioxidant activity ratings for olefin-alkylated diphenylamine in lubricating oil formulations (in neopentyl glycol ester base stock) has shown that the presence of n-alkyl radicals in the diphenylamine molecule has essentially no effect on the inhibiting activity of the amine, whereas the presence of a branched-chain radical reduces sediment formation in the oil when it is oxidized at 225°C for 10 h with an air feed rate of 50 ml/min through 50 g of oil in the presence of metal catalysts (Table 1). Such behavior of alkylated diphenylamines can be explained either by the difference in structure of the alkyl radical in the amine molecule or by a difference in its position on the benzene ring relative to the amine group. It is known from published information that, for example, alkylphenols with the alkyl substituents in the o- and p-position are not identical in reactivity with respect to peroxy radicals [1].

The work reported here was aimed at investigating the composition of alkylates that were obtained, and at ascertaining the structural difference of the components making up these materials, by methods of adsorptive separation, thin-layer chromatography (TLC), and IR spectroscopy.

The alkylation was performed as a Friedel–Crafts reaction with olefinic hydrocarbons (n-octane, n-nonene, and pure diisobutene). The characteristics of the alkylating agents are listed in Table 2. The methods used in the synthesis and in recovering the alkylate were described in [2].

For the TLC, the adsorbent was neutral chromatographic aluminum oxide of the second degree of activity, with a particle size < 325 mesh. The fixed layers were prepared from an aqueous suspension of the adsorbent with 5% gypsum. The ratio of water to aluminum oxide was 1.5 : 1. The layers were deposited by means of a Stahl instrument. Plates 130 × 180 mm with a deposited layer 360 μm thick were first dried 20 min at room temperature on a horizontal surface, then 3 h at 110°C.

TABLE 1. Antioxidant Activity of Alkyl Derivatives of Diphenylamine

Inhibitor	Characteristic of oil after oxidation		
	viscos. change, %	acid No., mg KOH/g	sediment, %
None	45,0	6,80	0,08
Diphenylamine	20,50	2,99	0,44
Octyldiphenylamine	17,00	2,10	0,50
Dioctyldiphenylamine	17,30	3,66	0,30
Nonyldiphenylamine	17,70	2,32	0,59
Isooctyldiphenylamine	22,80	2,19	0,03
Diisooctyldiphenylamine	22,50	2,90	0,02

All-Union Scientific-Research Institute for Petroleum Processing (VNII NP). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 1, pp. 50-54, January, 1974.

TABLE 2. Physicochemical Characteristics of Olefins

Hydrocarbon	bp, °C	Mol. wt.	Density ρ_4^{20}	Refrac. index n_D^{20}
n-Octene (99%)*	120—124	116	0,7148	1,4087
n-1-Nonene* (70% 1-nonene, 12% cis-2-nonene, 18% trans 2-nonene)	144—146	124	0,7290	1,4160
Diisobutene* (75% 2,4,4-trimethyl-1-pentene, 25% 2,4,4-trimethyl-2-pentene)	101—104	115	0,7187	1,4110

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*Hydrocarbon composition determined by gas-liquid chromatography.

TABLE 3. Composition of Alkylate Obtained in Alkylation of Diphenylamine by Hydrocarbons, as Determined by TLC

TLC characteristic $R_f \cdot 100$	n-Octene		n-Nonene		Diisobutene	
	alkyl derivative of diphenylamine	yield, %	alkyl derivative of diphenylamine	yield, %	alkyl derivative of diphenylamine	yield, %
67—69	o-Dioctyldiphenylamine	57	o-Dinonyldiphenylamine	16	—	—
64	Unidentified	Trace	Unidentified	Trace	—	—
51—53	—	—	—	—	Unidentified	Trace
47—48	o-Octyldiphenylamine	40	o-Nonyldiphenylamine	48	—	—
39	—	—	—	—	p-Diisooctyldiphenylamine	89
30					p-Isooctyldiphenylamine	10
26	Diphenylamine	2	Diphenylamine	25	Diphenylamine	Trace

TABLE 4. Physicochemical Characteristics of Alkyl Derivatives of Diphenylamine Separated by Adsorption

Alkyl derivatives of diphenylamine	Refrac. index n_D^{20}	mp, °C	Mol. wt.		Elemental composition, %					
					found			calc.		
			found	calc.	C	H	N	C	H	N
Octyldiphenylamine	1,550	—	278	281	85,90	9,96	4,08	85,41	9,61	4,98
Dioctyldiphenylamine	1,5224	—	387	393	85,80	11,30	2,90	85,49	10,95	3,50
Nonyldiphenylamine	1,5536	—	306	295	85,67	10,01	4,12	85,42	9,83	4,75
Dinonyldiphenylamine	1,5287	—	415	421	85,60	11,20	3,00	85,51	11,16	3,33
Isooctyldiphenylamine	—	47,5—48	273	281	85,90	9,72	4,48	85,41	9,61	4,98
Diisooctyldiphenylamine	—	101,5	387	393	86,02	11,00	2,91	85,49	10,95	3,66

At the start line of the finished plate, a 2-μm layer of a 2% benzene solution of the alkylate test sample was deposited by means of a chromatographic microsyringe. The chromatography was carried out by the ascending method in a crystallizer with a ground-glass cover for 50 min with a mixture of cyclohexane, benzene, and acetone in 10 : 1 : 0.1 ratio; each of the solvent components was purified on aluminum oxide before use. To detect the substances being analyzed, the plate was treated with iodine vapor.

From the TLC data (Table 3), it can be seen that the alkylates that were obtained represent multicomponent mixtures, in which each component is characterized by a constant value of $R_f \cdot 100$ for the given chromatographic conditions.

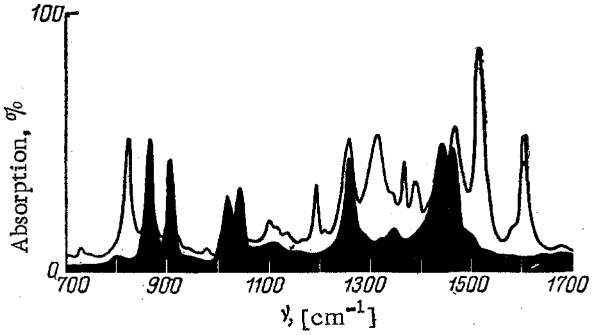

Fig. 1. Spectrum of diphenylamine.

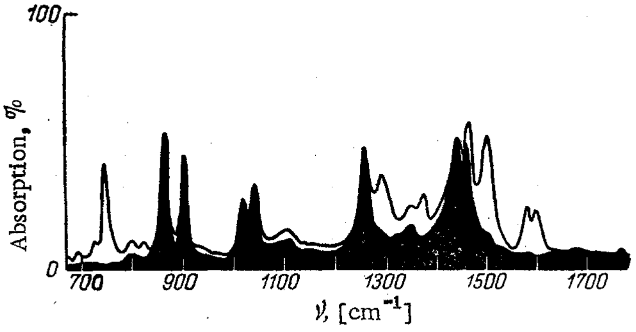

Fig. 2. Spectrum of dioctyldiphenylamine.

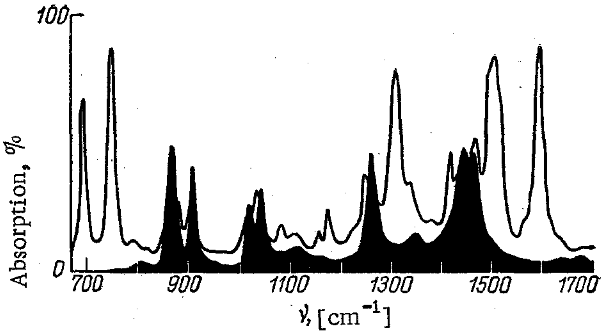

Fig. 3. Spectrum of diisooctyldiphenylamine.

By adsorption chromatography on Grade ASK silica gel, the alkylates were separated into constituents (in accordance with the values obtained for $R_f \cdot 100$) and were investigated by IR spectroscopy.

The IR spectra were taken in an IR-20 spectrophotometer in a solution of cyclohexane and carbon tetrachloride with partial (incomplete) condensation of the solvent in the second channel of the instrument. All spectra were taken under identical conditions. On each of the spectra of the test products, a solid-silhouette spectrum was superposed representing the solvent under the same conditions. The fractions recovered by adsorptive separation were also analyzed for elemental composition and molecular weight.

Compounds in the alkylated products characterized by $R_f \cdot 100$ values of 51, 53, 56, and 64 on the TL chromatogram were not identified, in view of the very small quantities (traces) that were available.

From determinations of molecular weight and elemental composition of the fractions of the n-octane alkylate characterized by $R_f \cdot 100$ values of 47 and 69, it was demonstrated that these fractions corresponded respectively to mono- and dialkyl derivatives of diphenylamine (Table 4). The IR spectra for these products indicate that the molecule of mono- or dialkyl derivative of diphenylamine contains alkyl substituents located in the ortho position with respect to the NH group. This interpretation is based on analysis of those changes occurring in the spectra of the indicated compounds in comparison with the spectrum of the unsubstituted diphenylamine (Fig. 1).

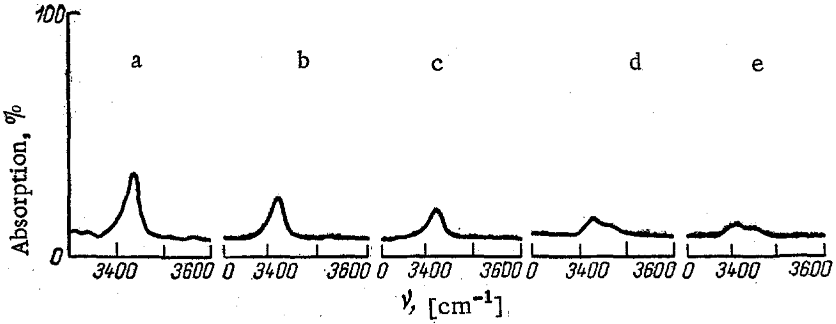

Fig. 4. Spectra of stretching vibrations of NH group for: a) diphenylamine; b) monoisooctyldiphenylamine; c) diisooctyldiphenylamine; d) monooctyldiphenylamine; e) dioctyldiphenylamine.

For example, the intensity of skeletal vibrations of the C = C bonds of the aromatic ring is significantly lower in the spectrum of the dioctyldiphenylamine (Figs. 2 and 3), which apparently indicates a breakdown of the conjugation of the benzene ring with the unshared electron pair of the nitrogen in the NH group, which is blocked by an alkyl substituent in the ortho position [3].

The band in the region of 690 cm^{-1} is entirely absent, and the unique absorption band in the region ~ 745 cm^{-1} indicates the presence of four neighboring hydrogen atoms in the benzene ring, which confirms the presence of an ortho substituent in the molecule.

The lower intensity of the absorption band in the 1300-cm^{-1} region is explained by the increase in mass of the molecule.

In the absorption region of stretching vibrations of the NH bonds (in the case of ortho-substitution), the band does not have the shape that is characteristic of unsubstituted diphenylamine (Fig. 4, curves a, d, and e); apparently here there is an influence of the formation of hydrogen bonds between the alkyl and the NH group.

The changes that have been noted in the spectrum of the dioctyldiphenylamine are somewhat less pronounced in the spectrum of the monooctyl derivative.

A comparison of the chromatographic behavior of the nonyl derivatives of diphenylamine with the corresponding octyl derivatives has demonstrated that they behave identically; thus, we can assume that these compounds are structurally identical. Hence, we can conclude that, in the alkylation of diphenylamine with straight-chain olefins, the predominant point of hydrogen replacement in the benzene ring is the ortho position.

The determination of molecular weight and elemental composition of the diisobutene alkylate components characterized by $R_f \cdot 100 = 30$ and 39 showed that these components correspond to mono- and dialkyl derivatives of diphenylamine. The IR spectra taken under the same conditions as for the other compounds confirm para substitution in the benzene ring. Evidence is found in the changes observed (for example) in the spectra of the diisooctyldiphenylamine (Fig. 3), where the band in the region ~ 825 cm^{-1}, which is characteristic for para substitution, is especially pronounced. The absorption bands in the 1500-1600-cm^{-1} region, similar to those in the spectrum of the unsubstituted diphenylamine, are very intense, since in para substitution the conjugation of the unshared electron pair of the amine nitrogen with the benzene rings is preserved.

Changes in the spectrum of the monoisooctyldiphenylamine are somewhat less pronounced than those in the dialkyl derivative.

The band for the stretching vibrations of the NH group for both compounds is similar in shape to that for the unsubstituted diphenylamine, but less intense (see Fig. 4, curves a, b, and c).

The spectroscopic data are closely related to the TLC data. In the IR spectrum of the unsubstituted diphenylamine in the region of skeletal vibrations of the C = C bond of the aromatic ring conjugated with the NH group, an intense absorption band is observed (see Fig. 1). The presence of an n-alkyl group in the o-position with respect to the NH group causes a strong shielding of the latter, which is expressed as a sharp reduction in intensity of absorption in the 1500-1600-cm^{-1} region in the IR spectra of the mono- and dialkyl derivatives (see Fig. 2), and in the thin-layer chromatogram as an increase in $R_f \cdot 100$ for these compounds (in comparison with the unsubstituted diphenylamine), i.e., by a decrease in adsorptivity of the molecule due to shielding.

The introduction of one or two isoalkyl groups in the p-position with respect to the NH group of the diphenylamine molecule gives hardly any disturbance of the coordination of the benzene rings with the NH group, so that the IR absorption bands in the 1500-1600-cm^{-1} region for the isooctyldiphenylamine are similar in intensity to those for the unsubstituted diphenylamine. In the thin-layer chromatogram for the isooctyl derivatives, this is expressed by the fact that the value of $R_f \cdot 100$ for the monoisooctyldiphenylamine is not significantly different from the value for the unsubstituted amine (see Table 3). When a second isoalkyl substituent is introduced, the value of $R_f \cdot 100$ increases somewhat. This same general influence of alkyl-substituent position (relative to the functional group) on the adsorptivity of aromatic molecules was observed for alkylphenol [4].

Thus, it has been revealed that the alkyl derivatives obtained by alkylation of diphenylamine with olefins of different structures (normal and branched) are not the same in structure; specifically, o-isomers predominate in the first case, p-isomers in the second.

SUMMARY

1. A study has been made of the composition of alkylates obtained by alkylating diphenylamine with various olefins, with the use of a combination of TLC, adsorption, and IR spectroscopy.

2. It has been shown that the alkylation of diphenylamine with straight-chain α-olefins produces mainly mono- and dialkyl derivatives that are described structurally as o-substituted secondary aromatic amines.

3. It has been shown that the alkylation of diphenylamine with branched-chain α-olefins produces mainly mono- and dialkyl derivatives that are described structurally as p-substituted secondary aromatic amines.

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