SPECTROPHOTOMETRIC EXAMINATION OF PURITY OF DIANE (4-4'-DIOXI-DIPHENYL-DIMETHYL-METHANE)

By

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The diane (4-4'-dioxi-diphenyl-dimethyl-methane) is a basic material of resins in the varnish industry. The dianes produced by different manufacturers may contain isomeric and metallic contamination in various quantities which may cause interference in the course of technological processes — resinification with epichlorohydrin to epoxy resin; then esterification with fatty acids.

So far the dianes have been quality tested by one of the following methods [1]: determination of phenol content, of melting point, colour test, determination of ash, water and iron content, as well as the determination of the colour of melt. However, the above data do not characterize sufficiently the quality of dianes.

Isomeric contaminants occurring in quantities of 0.1 to 2% can be determined by chromatography, but its application is lengthy and costly, since the measurement should be preceded by sililation.

The metallic contaminants appearing in trace amounts can be determined by atomic absorption method, prior to determination, however, destruction is necessary which makes its application more difficult.

Partly due to the above reasons, partly to the availability of cheap ultraviolet and infrared spectrophotometers suitable for routine analyses — a simple photometric method has been elaborated for the quality testing of dianes.

Experimental

Examination of isomeric contaminants

The isomeric contaminants of industrial dianes are as follows (Fig. 1): 1,1'-dioxi-diphenyl-dimethylmethane (ortho-contaminant), 1,4'-dioxi-diphenyl-dimethyl-methane (ortho-para-contaminant), phenol and sometime tris-pheno (para-contaminants). They amount from 0.1% to 2% by weight. In this paper the first three contaminants are dealt with. The method chosen for their determination was infrared spectroscopy.

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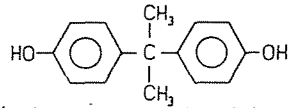
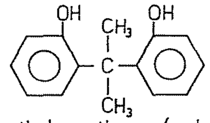
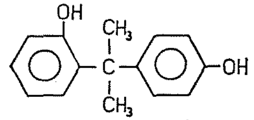


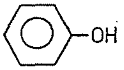
diane (4-4'-dioxi-diphenyl-dimethyl-methane)



1-1-dioxi-diphenyl-dimethyl-methane („orho-contaminant")



1-4'-dioxi-diphenyl-dimethyl-methane („ortho-para contaminant")



phenol

Fig. 1. The structure of diane and its main contaminants

The infrared spectra of 26 different industrial dianes have been prepared and compared to diane spectra found in the literature [2].

The spectra were taken with IR spectrophotometer (Type Zeiss UR-10) applying potassium bromide measuring technique. The IR spectra of dianes examined by us showed good agreement with those found in the literature regarding the number and place of absorption bands. Deviation was detected only in the change of intensity ratio of certain bands, which served for the quantitative characterization of isomeric contaminants in the way described below.

In Fig. 2, the spectrum of a Japanese diane is seen, serving as a standard to our examinations, since previously its ortho-, ortho-para and phenol contaminants have been measured at 0.1%. In the case of other dianes this quantity is usually higher, although it does not exceed 1—2%. Remind that the IR spectral bands do not show contaminants occurring in such small quantities and the quantitative analysis by IR spectroscopy can be realized only in the

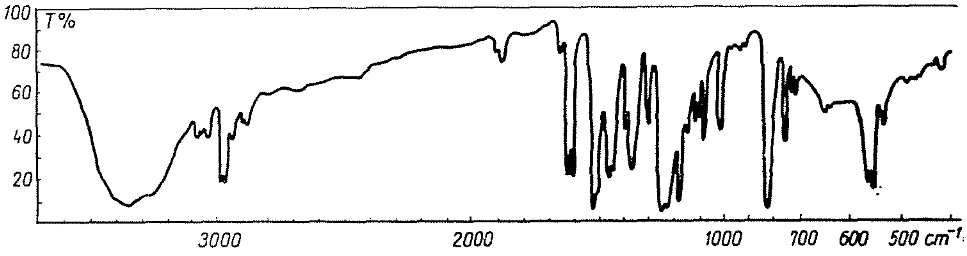


Fig. 2. IR spectrum of diane

Table I

Interpretation of IR bands of dianes

Absorption place (cm^{-1})	Interpretation	Absorption place (cm^{-1})	Interpretation
3350	ν OH	960	γ (=CH), 17a
3050	ν (=CH), 7b	920	γ (=CH), 5
3070	ν (=CH), 2	828	γ (=CH), 11
3030	ν (=CH), 20b	758	β CC, 6a
3020	ν (=CH), 20a	740	γCC, 4
2978	ν_{as} CH_3	758	β CC, 12
2968	ν_{as} CH_3	645	β CC, 6b
2930	ν_{as} CH_3	565	γ CC, 16b
2870	ν_s CH_3	555	β CC, 12
1650	overtone	530	β (=CH), 9b
1620	ν CC, 8a	420	
1608	ν CC, 8b		
1520	ν CC, 19a		
1452	δ_{as} CH_3		
1442	ν CC, 19b		
1390	ν CC, 14		
1370—45	δ_s CH_3		
1302	β (=CH), 3		
1240	β OH		
1222	ν (=CH) 7a		
1182			
1152	β (=CH), 9a		
1120	β (=CH) 13		
1105	β (=CH) 18b		
1090	breathing 1		
1020	β (=CH) 18a		

Legend: ν stretching vibration
subscripts as, *s* symmetrical, asymmetrical, resp.
δ bending vibration
β bending vibration in plane
γ bending vibration out of plane
Arabic numerals and small letter: Wilson numbering

case of main components. Therefore another way of quantitative characterization has been chosen, i.e. observation of the intensity ratios of certain bands. First of all, however, the spectrum of diane should briefly be interpreted (Fig. 2). The explanation of bands was based on VARSÁNYI's work [3, 4] and compiled in Table I.

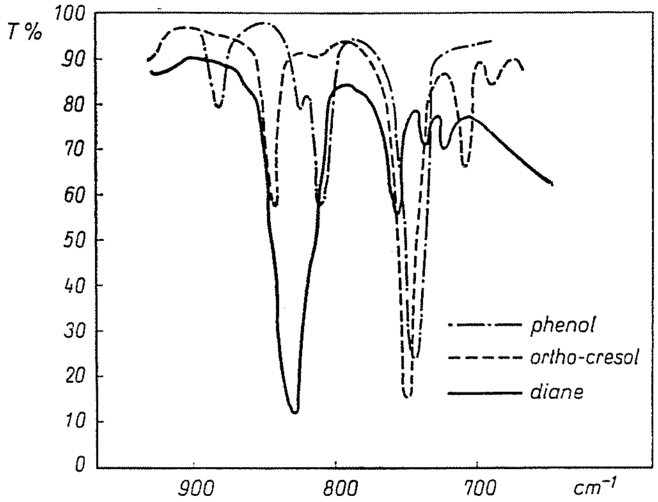


Fig. 3. Section from the IR spectrum of diane and its contaminants

In the case of all dianes the spectral bands appear in the same number and place, in a range characteristic of the substitution of aromatic rings (between 900—700 cm^{-1}) depending on their isomeric contamination with changed intensity ratio. The question is, the intensity of which bands is influenced by the single isomeric contaminants. Literature data [3, 4] and the IR spectra of the chosen model compound phenol and ortho-cresol taken by us (Fig. 3), as well as the changes observed in the spectra of diane provided conclusions for the above question. It has been stated that the intensity of the diane band appearing at 758 cm^{-1} is influenced by the ortho-, ortho-para-isomers and phenol, while in the band appearing at wave number 828 cm^{-1} these components do not cause considerable interference (Fig. 3). For this reason the extinction of the band at wave number 758 cm^{-1} has been compared to that at 828 cm^{-1} (Fig. 4). The quotient $\frac{E_{758\,\mathrm{cm}^{-1}}}{E_{828\,\mathrm{cm}^{-1}}}$ refers to the quantity of the discussed contaminants. Extinctions have been determined by baseline correction from the expression (Fig. 4):

$$E = \log \frac{I_0}{I} \, .$$

For the classification of samples a ratio has been defined. The diane, No 24 was chosen as a basis with known isomeric contamination (0.1%), showing optimal qualities in the course of technological processes. With this diane, the above extinction quotient was taken as 100%, and the quotients of the other dianes were referred to it. Our measuring results are summarized in Fig. 5.

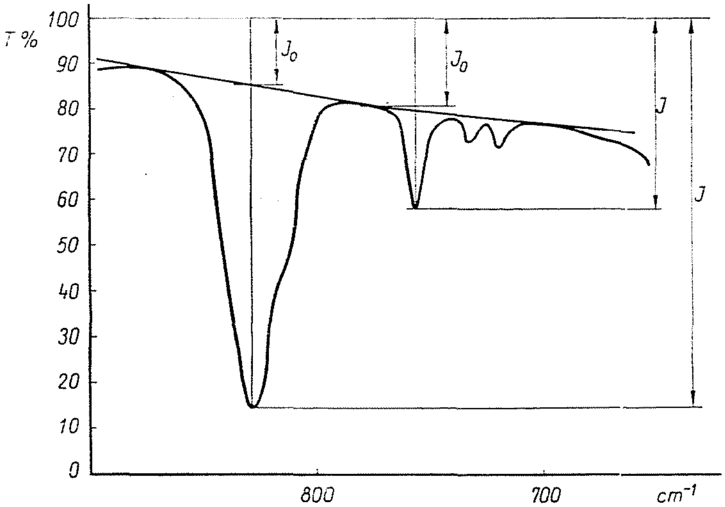


Fig. 4. IR spectrum section of a sample in the evaluable range of bands

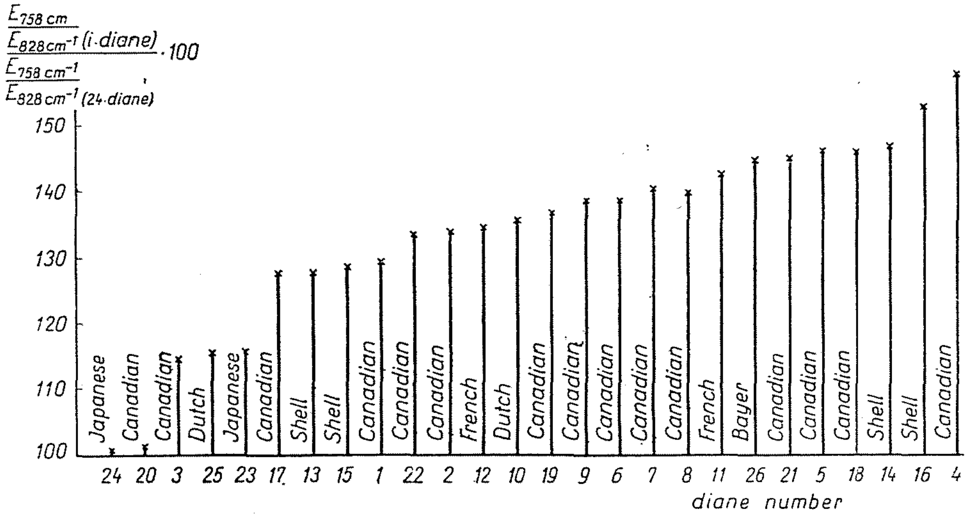


Fig. 5. The parameter referring to the quantity of isomeric contaminants in the test samples

On the vertical axis the quotient $\frac{E_{(758\ \mathrm{cm}^{-1})}}{E_{(828\ \mathrm{cm}^{-1})}}$ was plotted against the percentage of diane 24. The "ranking" obtained this way showed a good agreement with the behaviour of dianes displayed in technological processes, rating the fineness of dianes, namely, the closer the number to hundred, the clearer the diane. If the ratio is between 100—130, the diane is still convenient, above 130, however, some irregularities may occur in resinification.

The ratios defined by us have been compared to data measured by some gas-chromatographic methods, also semi-quantity conclusions may be drawn regarding the percentage of isomeric contaminants.

The value of 100 corresponds to 0.1% isomeric contamination, while 150 to 160 refers to about 2% isomeric contamination. Accordingly, dianes are simple to be quality tested:
Drops of 7 mg sample/1 g potassium bromide concentration both from the standard and the diane to be tested were prepared, their IR spectra taken in the interval of 900—700 cm^{-1}, the extinction ratio of bands at wavenumbers 758 and 828 cm^{-1} was determined, then the value for the sample examined was expressed as a percentage of standard diane ratio. If the value obtained is below 130%, then the diane is suitable for resinification, else the technological process may be disturbed.

Examination of metallic contaminants

Metallic contaminants Na, Ca, Cu, Si, Mg, Al, Fe, Mn, Zn may be found in dianes in the concentration range 0.01—10 ppm. Instead of the atomic absorption method which requires previous destruction, a simple method — convenient for routine analytical purposes — was elaborated for determining the amount of metallic contaminants. The empirical fact was taken into consideration that dianes — containing metallic contamination in a higher quantity than permitted — show a tawny colour in alkaline solution and the intensity of colour increases with time. This browning is presumably owed to some oxidation process catalysed by the metallic contaminants of dianes. Thus, the time-dependence of browning can be stated to be different for different dianes. According to our assumptions the more the metallic contamination in diane, the stronger the colour after a given period of time. These assumptions have been justified by our measurements. Let us outline first the information concerning the UV-VIS spectrum of dianes. Spectrophotometer (Type Unicam SP 700) recordings were made on a solution of 0.005% diane and 0.01% potassium hydroxide in a cuvette of 1 cm in the range of wavenumbers 55 000—15 000 cm^{-1}. In Fig. 6 the spectrum of one of the dianes examined is seen. The spectra of each sample were found to be similar. In the UV range 3 bands occur at wavenumbers 47 200, 41 050 and 34 400 cm^{-1} which can be originated from the $\pi - \pi^*$ transitions of aromatic rings. In such a weak solution the spectrum does not change as a function of time, the diane shows no change in colour, in the visible range there is no absorption. In concentrated solutions, however, (5% diane in 10% potassium hydroxide solution) a stronger or weaker browning could be observed depending on the quality of dianes. In the coloured solutions a new band appeared in the visible range — even the bands in the UV region altered their outline — and the band

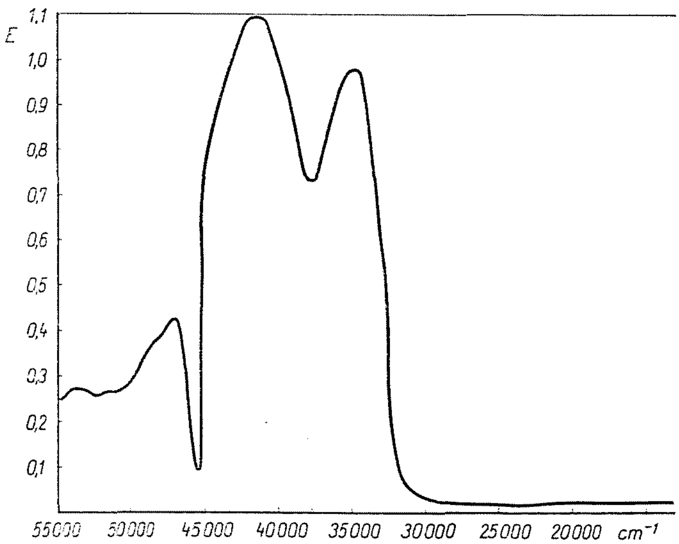


Fig. 6. UV-VIS spectrum of diane

intensity increased with time. This served as basis to our measuring method performed as follows: strong alkaline solutions of dianes have been prepared, then their spectra regularly taken in a 1 cm cuvette at wavenumbers 30 000—13 000 cm^{-1}, where at wavenumber 21 100 cm^{-1} a band characteristic of the brown colour appeared. The degree of browning was determined as follows: spectra taken of dianes at different times were superimposed (Fig. 7 shows diane No. 16), pointing out which dianes brown more strongly. Also extinctions at 21 100 cm^{-1} at different times were plotted.

Figure 8 shows the colour of diane No. 16 to have darkened during 168 hours from the preparation of solutions and to clear during the following 24 hours. Similar phenomenon is expected in the case of other dianes, although sometimes the colour darkened even after 168 hours. The rise of the curve on the diagram is characteristic of the rate of darkening. Its value shows little change at different times. The expression below has been defined as numerical characterization:

$$\text{Index} = \frac{E_{168} - E_0}{t} = 0.006\,(E_{168} - E_0)\ \text{hour}^{-1},$$

where

E_0 : extinction after preparing the solution, at wavenumber 21 100 cm^{-1},
E_{168} : extinction after 168 hours, at wavenumber 21 100 cm^{-1},
t : 168 hours.

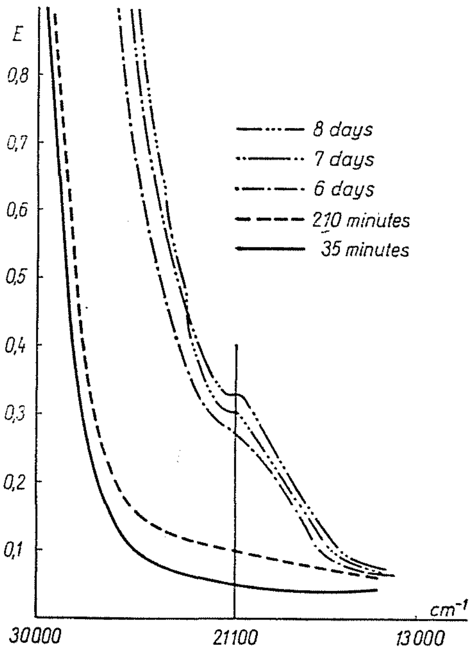


Fig. 7. The time-depending change of the UV-VIS spectrum of a diane sample

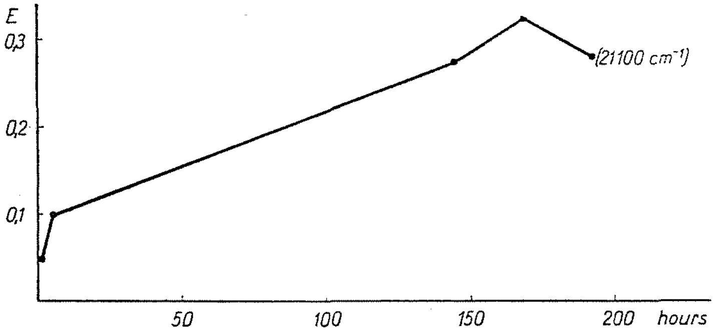


Fig. 8. Extinction-time correlation to follow the browning process of a diane sample

Indices of the individual dianes calculated in this way are presented in Fig. 9. Here no comparison was made to the standard, but the samples were listed in the increasing order of indices. The samples about free of isomeric contaminants are seen to contain metallic contaminants in a higher quantity, than dianes of some other origin. The order set up by us was lately supported also by atomic absorption measurements. A subsequent paper will present numerical correlation between these data and indices we defined.

As a conclusion it can be stated that in lack of atomic absorption apparatus, the metallic contamination of dianes can be detected also by spectro-

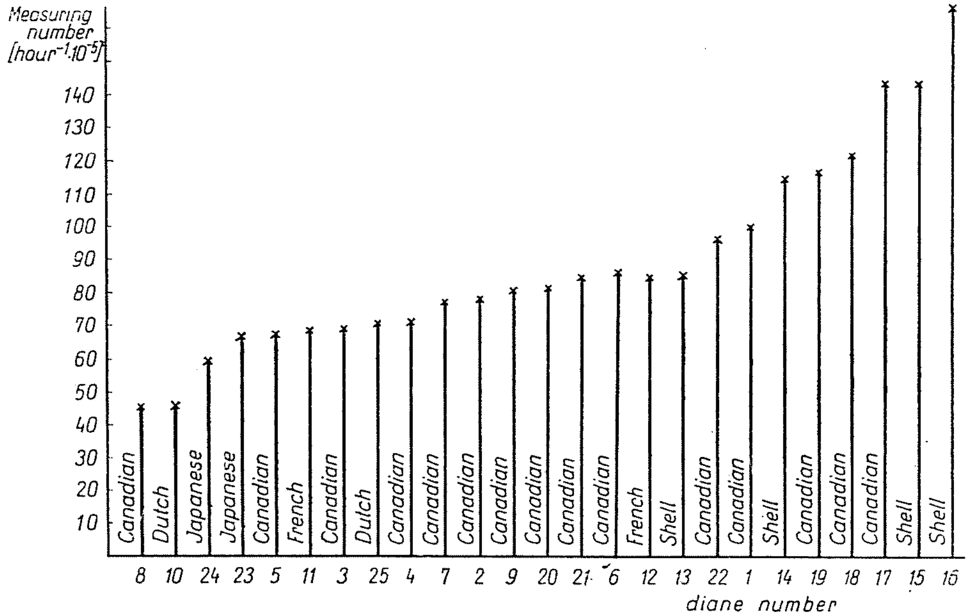


Fig. 9. Browning index of dianes on the basis of extinctions at wavenumber 21 100 cm^{-1}

photometric method preparing a 5% diane solution with 10% potassium hydroxide determining the extinction of solution in a cuvette of 1 cm immediately and after 168 hours. The difference between the two extinctions divided by 168 is a characteristic index. Dianes exhibiting indices below $7 \cdot 10^{-4}$ were seen to behave regularly in technological processes but above this value some irregularities may occur during resinification. The advantage of the method lies in its simplicity, somewhat offset, however, by the fact that 168 hours are needed to pass between the two extinction measurements in order to get well evaluable differences. This drawback is tolerable, since the diane shipments are never processed instantly, so there is time enough to carry out the above, extremely simple test.

Summary

A method has been elaborated for the spectrophotometric purity examination of diane (4-4'-dioxi-diphenyl-dimethyl-methane). The isomeric contaminants were measured by infrared spectrophotometric method. The intensity of the spectral band appearing at wavenumber 758 cm^{-1} is influenced by the ortho-, ortho-para- and phenol contaminants, while that appearing at 823 cm^{-1} seems not to be influenced. Thus, the ratio of the extinctions of these two bands compared with the value of a standard pure diane — provides for characteristic data about the quantity of isomeric contaminants, and about the expected behaviour of diane in the course of technological processing. The metallic contaminants of dianes have been observed to catalyse the browning process of the alkaline solutions of dianes. On this basis, from the extinction change of the band at wavenumber 21 100 cm^{-1}, characteristic of the brown colour in unit time, the metallic contaminants can be concluded on.

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