

Ultraviolet Spectra of Elastomers and Rubber Chemicals

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ULTRAVIOLET SPECTRA OF ELASTOMERS AND RUBBER CHEMICALS

ATLAS UL'TRAFIOLETOVYKH SPEKTRON POGLOSHCHENIYA VESHCHESTV,
PRIMENYAYUSHCHIKHSYA V PROIZVODSTVE SINTETICHESKIKH KAUCHUKOV

АТЛАС ультрафиолетовых спектров поглощения веществ,
применяющихся в производстве синтетических каучуков

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PREFACE

In the modern organic synthesis industries, one of which is the synthetic rubber industry, ever increasing use is made of physical and physicochemical methods of analysis, which surpass chemical methods in speed, accuracy, and sensitivity. By these methods it is often possible to arrive at the solution of problems in the investigation of complex mixtures of organic products which are not amenable to the usual chemical methods of analysis.

One such physical method is ultraviolet spectrophotometry. The field of application of this method is restricted, in the main, to aromatic compounds and to systems containing double bonds conjugated among themselves or with functional groups. In the synthetic rubber industry ultraviolet spectroscopy finds application in the analysis of a great variety of substances used in that industry: for the determination of impurities in monomers and intermediate products, in the study of the composition of certain polymers, for the quantitative estimation of various ingredients in rubbers, in the control of certain copolymerization processes, and for many other purposes. The method can be used for the identification of certain compounds and can be applied in the determination of the composition of synthetic rubber samples. Shortcomings of the method, which limit its analytical application in certain cases, are the superposition of absorption spectra and their inadequate selectivity.

The atlas gives absorption spectra in the near ultraviolet (200–400 $m\mu$) for 141 different substances met in synthetic rubber manufacture: monomers, polymers, various antioxidants, and other substances used in the synthesis of rubbers (emulsifiers, initiators, regulators, various auxiliary materials, etc.).

All the spectra are represented in the form of graphs of

the relation $\alpha = f(\lambda)$, in which α is the specific extinction coefficient (optical density of a solution containing 1 g of the substance in 1 liter at a layer thickness of 1 cm) and λ is wavelength ($m\mu$). The scales of the spectra vary: they were chosen so as to reveal the characteristics of the spectrum as clearly as possible. The spectra shown in the atlas were determined by the authors in the laboratories of the All-Union Synthetic Rubber Research Institute with an SF-4 spectrophotometer at room temperature ($20 \pm 3^\circ\text{C}$). Many of them were determined for the first time. The relative error in the determination is up to 5%, which is usual for the SF-4. In some cases our results do not agree with data in the literature (which are cited in footnotes to the tables). It should be noted that in a number of cases we had to deal with technical products or with substances of unknown purity. This refers mainly to antioxidants and to various ingredients used in the synthesis of rubbers.

Apart from the spectra, at the beginning of each section a table is given which states the solvent in which the measurement was conducted, the wavelength λ_{max} at each absorption maximum, and the specific α and molecular ϵ extinction coefficients at each maximum.

In the legends to the figures we state, successively, the solvent, the concentration c , and the thickness d of the layer of solution.

The atlas does not give the spectra of some aromatic hydrocarbons used in the synthetic rubber industry as solvents or for other purposes (e.g., benzene and toluene) because their spectra can be found in a readily available atlas [1]. The general laws of electronic spectra and the experimental techniques, which have been described in the literature [2, 3], are not expounded here.

The authors hope that, despite possible shortcomings, this atlas will be found useful in the practical work of spectroscopists, not only in the synthetic rubber industry, but in allied fields (plastics, petrochemicals, etc.) in which the compounds whose spectra are given in the atlas can be met.

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I. MONOMERS

The monomers used in the preparation of synthetic rubbers (Table 1) are substances containing a system of conjugated double bonds or a double bond conjugated with a triple. The absorption spectra of all of them therefore contain strong K bands. When the substance contains a double bond conjugated with a benzene ring, a B band appears in addition to the K band. When the double bond is conjugated with a carbonyl group (acrylic compounds), the K band is considerably weaker.

The character of the absorption spectrum is also affected by the substituents situated at the conjugated bond. When there is a substituent on the second carbon atom of a dienic system, a bathochromic shift in the absorption band is observed (isoprene, chloroprene). Also, substituents such as methyl or chloro bring about a reduction in the strength of the absorption band. When the methyl group is on the first carbon atom of the dienic system a bathochromic shift in the absorption band is again observed, and there is a still greater reduction in its strength (piperylene). A methyl group on the second carbon atom at a double bond conjugated with a benzene ring brings about only a slight reduction in the strength of the two bands (K and B), but in this case there are hypsochromic shifts in the absorption bands (α -methylstyrene).

When the double bond is conjugated with a pyridine ring, the strengths of the K and B bands are much lower than in the case of conjugation with a benzene ring, and the absorption bands are shifted considerably toward the longer waves.

Since the polymerization of a monomer destroys the conjugated system of bonds, polymers do not give K absorption bands. It is therefore possible to estimate the amount of unchanged monomer from the strength of the absorption band and to follow the progress of the polymerization. Similarly, the residual monomer content of a polymer can be determined spectrophotometrically [4].

MONOMERS

TABLE 1
SPECTRAL CHARACTERISTICS OF MONOMERS

Figure	Monomer	Solvent	λ_{\max} , $m\mu$	α	ϵ
1	1,3-Butadiene	Ethanol	218	570	30,750*
2	Isoprene (2-methyl-1,3-butadiene)	Ethanol	223	316	21,500†
3	Chloroprene (2-chloro-1,3-butadiene)	Ethanol	223	240	21,250
4	Piperylene, 93% of <i>trans</i> form (<i>trans</i> -1,3-pentadiene)	Ethanol	220	250	16,850‡
5	Piperylene, 77.5% of <i>cis</i> form (<i>cis</i> -1,3-pentadiene)	Ethanol	225	235	16,000‡
6	Styrene	Ethanol	208	203	21,100
			248	150	15,500§
7	α -Methylstyrene	Dioxane	248.5	137	14,300
			206	170	20,000
8	Methacrylic acid	Ethanol	207.5	92	7,900
9	Methyl methacrylate (technical)	Ethanol	207.5	84	8,400
10	Butyl methacrylate (technical)	Ethanol	207.5	66	8,300
11	Acrylonitrile	Ethanol	205	90	4,750
12	2-Vinylpyridine	Chloroform	238	109	11,450
			278.5	48	5,050
13	5-Vinyl-2-picoline	Chloroform	244	140	16,650
			284	37	4,400
14	2-Methyl-5-hexen-3-yn-2-ol	50% Ethanol	221.5	138	15,200
			230.5	111	12,200
15	<i>p</i> -(1,1-Dimethyl-4-penten-2-ynyl)phenol	50% Ethanol	223.5	107	19,900
			275.5	10	1,850

*In hexane λ_{\max} = 217 $m\mu$, ϵ = 20,900 [5].

†In hexane λ_{\max} = 220 $m\mu$, ϵ = 23,900 [5]. In hexane λ_{\max} = 220 $m\mu$, ϵ = 21,000 [6].

‡In alcohol λ_{\max} = 223.5 $m\mu$, ϵ = 23,000 [8].

§In alcohol λ_{\max} = 244 $m\mu$, ϵ = 13,000 [9].

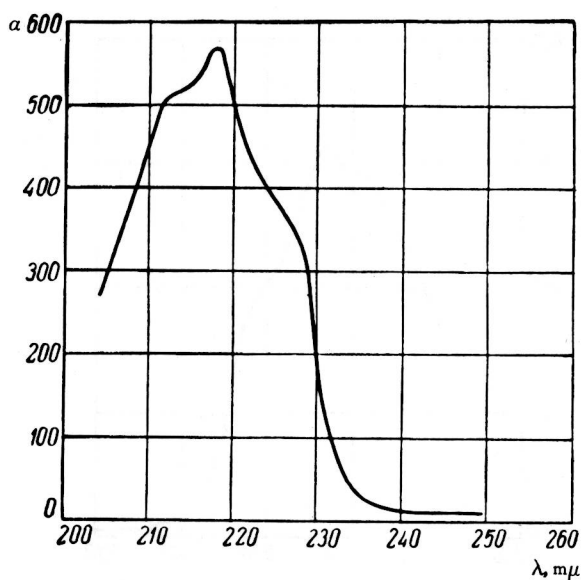


Fig. 1. 1,3-Butadiene

$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$

Ethanol
 $C = 0.15 \text{ g/liter}$
 $d = 0.58 \text{ mm}$

MONOMERS

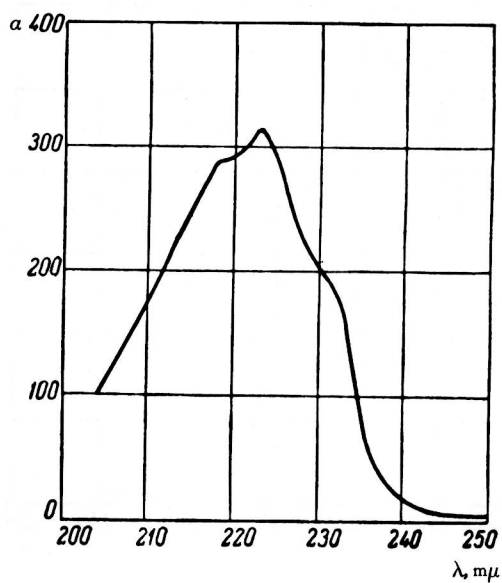
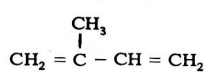


Fig. 2. Isoprene (2-methyl-1,3-butadiene)



Ethanol
 $C = 0.15 \text{ g/liter}$
 $d = 0.58 \text{ mm}$

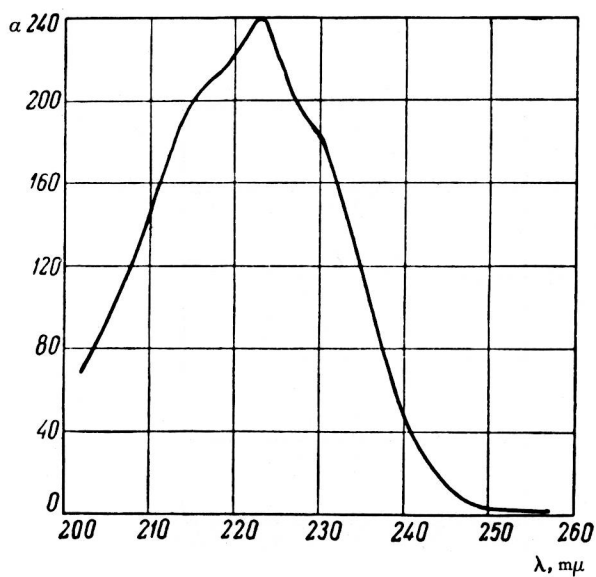
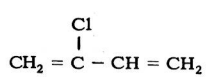


Fig. 3. Chloroprene (2-chloro-1,3-butadiene)



Ethanol
 $C = 0.82 \text{ g/liter}$
 $d = 0.058 \text{ mm}$

MONOMERS

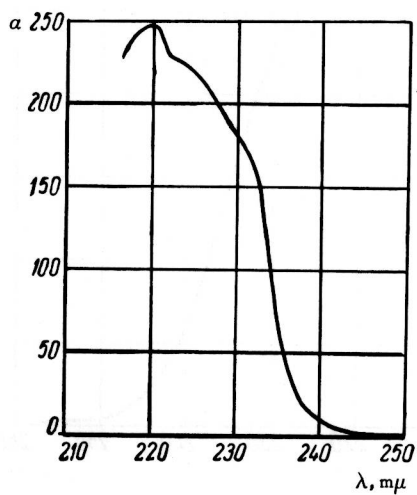
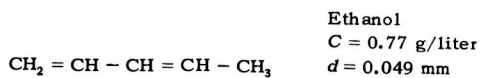


Fig. 4. *trans*-Piperylene (*trans*-1,3-pentadiene)



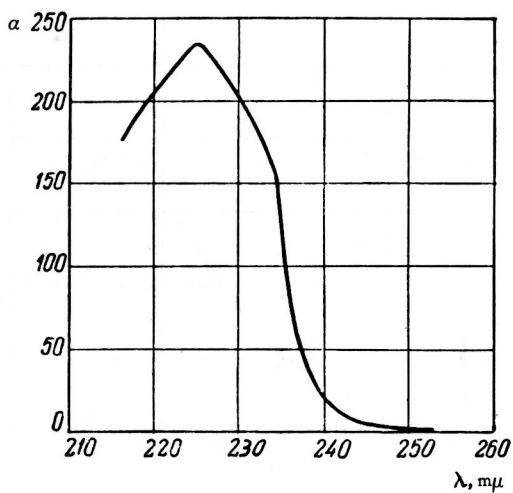
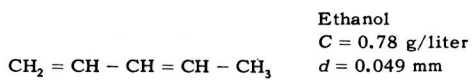


Fig. 5. *cis*-Piperylene (*cis*-1,3-pentadiene)



MONOMERS

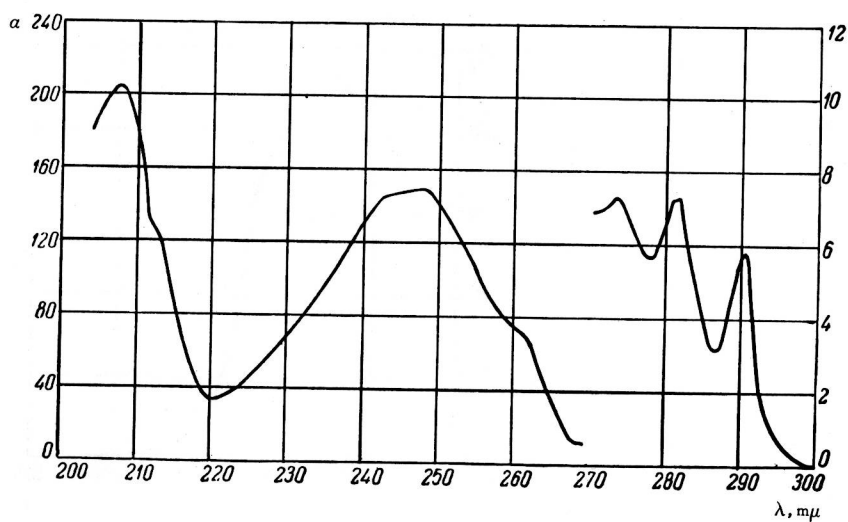


Fig. 6. Styrene

$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$

Ethanol
 $C = 1.06$ g/liter
 $d = 0.058$ and 1.004 mm

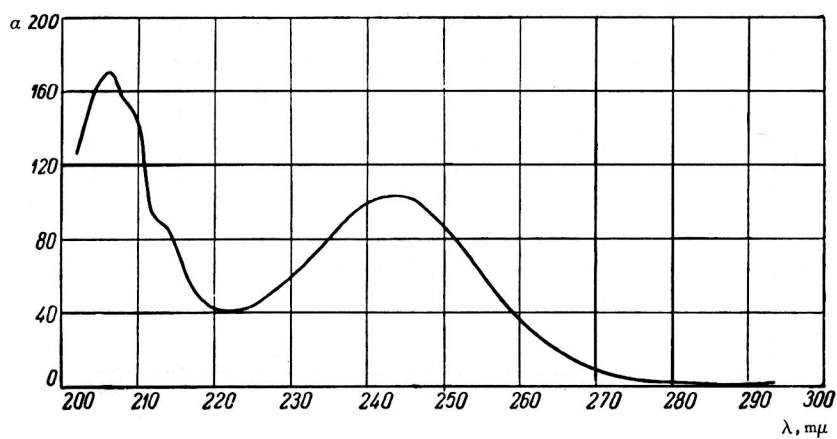
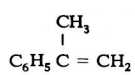


Fig. 7. α -Methylstyrene



Ethanol
 $C = 1.016 \text{ g/liter}$
 $d = 0.058 \text{ mm}$