THE USE OF THERMO-MECHANICAL AND MORPHOLOGICAL ANALYSES FOR RESEARCH ON PROPERTIES OF BITUMINOUS COMPOSITIONS

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In an effort to study structure and parameters of bituminous polymeric composites, it is supposed the use of the automated system of qualitative morphological analysis (QMAS) will allow the substitution of conventional subjective methods of visual examination by means of digital data handling of the objects images. This method ensures the acquisition of statistically reliable information on sizes of structure elements (polymer or bitumen domains), form factors, coordination numbers and on the distribution according to these parameters.

The application of QMAS obtains a "structure-properties" and "technology-structure-properties" relationship which optimizes composition and technological parameters of the composition manufacture. The examples of QMAS application have been presented for research in the manufacturing technology of bitumen and rubber crumbs mixtures.

The application of thermo-mechanical and dilatometric analyses for the investigation into bitumen properties have been proposed and that of its components resolved by conventional chromatographic methods.

KEYWORDS

Bituminous polymeric composites, qualitative morphological analysis, thermo-mechanical, dilatometric analysis.

INTRODUCTION

The vast territory and climatic features of various regions of the USSR dictate the use of a sufficiently wide range of sheet bituminous polymeric roofing materials with a variety of properties. This reason and that of the deficiency of the conventional modifiers—APP and SBS—in the USSR necessitate the wide use of certain polymers as modifiers that are generally not used for this purpose (e.g., low-molecular polyethylenes, rubber crumbs—industrial or usage waste, etc.).

The use of low-efficient types of modifiers, as well as APP and SBS (but in lower than usual concentrations), predetermines that increased requirements to the homogeneity of bituminous polymeric systems.

It is common knowledge that physico-mechanical and performance properties of bituminous - polymeric composites (BPC), and hence their reliability and durability, depend on the nature and content of the components, structure and texture features of the composition determined to a large extent by its production technological parameters.

Main differences of the methods applied for BPC structure and texture studies are associated with the varieties in geometric dimensions of the studied formations. As a rule the latter makes up no less than $10^2 \cdot 10^3$ (tens · hundreds of Angströms in the case of structure-forming elements; microns and the larger ones · in the case of a texture). Therefore, if BPC texture studies lie primarily in the analysis of the visually observed objects (to be sure with the use of special devices of optical and electronic microscopy), then research into BPC structure organization presupposes interpretation of the indirectly obtained data (e.g., by means of small-angle diffraction of Roentgen rays).

BPC samples predetermine the visualization of the optical magnification up to sizes permitting the authors to distinguish elements of interest. Performing structural studies by means of electronic microscopy necessitates the use of faster-type installations permitting optical resolution of objects with sizes less than 10^{-2}mm. Negatives in using this informational method for BPC study follow:

- The difficulties of sample preparation consisting particularly in spraying of the metal layer on a fracture surface of a sample.
- The complexity and the high price of equipment.
- The probability of preparative changes as well as changes in the survey process under the influence of electronic pencil.

In textural researching, visualization can be ensured in two ways: photomicrography with the use of an optical microscope and/or photomacrography when optical magnification corresponds to a summary photomagnification at survey and printing. In the first case, the magnification increases up to $X10^3$, and in the second by an order of lower magnitude.

In some cases photomicrography and photomacrography can complement each other: the former is characterized by the small definition in depth of the photographic image sharpness and obtains a series of layer-by-layer images of the preparative; photomacrography featuring considerably larg-

er definition in depth of sharpness ensures the possibility of the view images giving an idea of a sample as a whole.

It is well-known that bituminous polymeric compositions are the heterogeneous systems. The polymer swelled in malthenes is a dispersed phase of them. Forms, dimensions and the relative positions of the constituent elements of the dispersion can vary greatly. Among other things BPC properties significantly depend on these structural parameters; clearly the smaller a polymer particle diameter, and the more evenly it is distributed in a bituminous matrix, the larger extent of the polymeric specific properties use and the better qualities of the composite. In this respect, the possibility of the qualitative evaluation of the bituminous polymeric systems texture parameters assumes the distinctive importance. Evidently, the most simple evaluation method is the analysis of the BPC sample image obtained by means of some standardized preparation procedure (within one experimental series at any rate).

In general, the obtained BPC preparation image takes into account one or another feature of the material textural character which doesn't allow for a correct and especially qualitative textural analysis as the visual information represents the entire complex of various elements. Primarily, this prevents the wide use of the method in BPC development.

To solve this task, the authors propose the use of the automated system of qualitative morphological analysis (QMAS). The proposed system comprises a microelectronic computer "Iskra-226" with 128 kilobytes of memory equipped with a black and white built-in display for representation of alphanumeric and graphic information, and a stand-by input/output, including: TV camera "Electronika-823"; raster electronic microscope "Telsa BS-340"; graphic matrix printer "Robotron-1154"; optical microscope "Biolar"; videocontrol unit, and external memory devices on magnetic discs.

The system is equipped with the software for correction, transformation and analysis of the images.

The QMAS software permits input of the object images from raster electronic or optical microscopes, TV cameras, the reading image from magnetic carriers, the calculation of brightness histograms, performing correction of semitone image against one signal level, automated transformation of the image to a binary one, analyzing orientation against a semitone image and analyzing morphology against binary image.

QMAS provides acquisition of the statistically reliable data on the size of BPC structure elements—mean diameter, perimeter and area of a polymer or bitumen domains, form factor, coordination number, etc.

In addition, the QMAS procedure contemplates the acquisition of the data on the distribution of the studied structure elements according to the above-mentioned parameters.

The performed research into test objects (drawings depicting the predetermined quantity of objects of a certain geometric configuration) pointed to the fact that the acquisition of the statistically reliable data on the real object texture requires treatment with the use of an analyzer of no less than $p.10^2 (1 \blacktriangleleft n \blacktriangleleft 10)$ elements relating to one sampling. Simultaneous input into QMAS of such quantities of elements of a complex configuration and with more bound into a single space formation presents difficulty due to the effect of discreetness and to the limited inspection field of the used equipment (128 X 128 bytes). Therefore, the procedure used presupposes the scanning along the image plane of a preparation as far as the accumulation of the statistically reliable data. In practice, it indicates the examination from 10 to 20 separate sections (fields) of each studied sample.

Below are examples of the operation sequence and the results of morphological analysis of BPC micropreparation representing the mixture of a low-blown bitumen and rubber crumbs (rubber crumbs content is 15 weight percent, average crumb particle size is 1.2mm). The mixture was prepared in a heated mixer with a screw mixing device (rotational speed 200 r/min.). For this purpose bitumen heated to 180°C with the softening temperature of 50°C was loaded into a mixing reservoir. Afterwards, portions of necessary quantities of rubber crumbs were added. The mixture was agitated for one hour at 170°C.

Figure 1 displays photos of the analyzed fields images of BPC micropreparation obtained with the use of the optical microscope "Biolar," with X5 magnification the images were input into EC memory with the use of the load module.

Figure 2 depicts a view of a semitone image of the field N 1. The objects examined—particles of the swelled in bitumen malthenes rubber—are a black color. Further, the starting semitone image is transformed into a binary one. Owing to the presence of noise resulted from imperfection of the data input system, binary images are distorted (Figure 3). Successive images of the field N 1 of a preparation obtained in the process of correction by special QMAS modules are presented in Figure 4. The resulted distortion-free images of the studied fields of the preparation are displayed in Figure 5.

Further, the binary image recorded on a magnetic disc is analyzed by QMAS processing module.

The module work comprises "the round" of the image to detect some element (pore or particle), the "round" along the boundary of the element (in doing so, perimeter $\underline{P}$ is being calculated) and "the removing" (erasure) of the element to exclude it from the repeated analysis (in doing so, element area A is being calculated). The size of the element is calculated as a diameter of a circle with equivalent area:

$$D = \sqrt{\frac{4A}{\pi}},$$

form factor K is computed from the formula

$$K = \frac{4\pi A}{\underline{P}^2}.$$

In the course of analysis, the forming of a table depicting parameters of the individual particles takes place.

The totality of the above-mentioned parameters that QMAS obtains provides an adequate qualitative BPC texture and structure description. It also achieves a "structure - properties" relationship and that of structural and technological parameters as well (e.g., "average polymer particle diameter - dispersion time" or "apparatus type - average particle size," etc.).

By this means, QMAS application optimizes composition and technological parameters of BPC manufacture.

As an example of QMAS application optimizing composition and technological parameters of BPC manufacture, consider the results of morphological analysis of a series of BPC samples.

Tables 1-3 list the results of morphological analysis of BPC samples, obtained from the mixing of bitumen and rubber crumbs—the product resulting from milling worn tires. The

initial ("unaged") rubber contained cured butadiene-methylstyrene rubber of SKMS - 30 ARKM - 15 grade (about 60 percent, filler - technical carbon (about 30 percent), paraffin, zinc oxide, stearic acid, antioxidants (neozon D) and some other ingredients. In all cases, the mass share of rubber crumbs accounts for 20 percent, the average diameter of the starting crumbs is 276mm, and the mixing temperature is 210°C.

As is seen from Table 1, using a plasticator (mean diameter, D_m, and mean form factor, K_m) of the rubber crumbs decreases monotonously with the increase of the mixing duration, the distribution of particles in size change from bimodal to unimodal. The above-mentioned changes are accompanied by the improvement of the composition properties.

In Table 2, the analysis results of samples obtained in apparatuses of various constructions are given. The plasticator is a mixer containing two parallel rotors being in contact with each other and manufactured in disc form with teeth. It being known that working surfaces of the rotors form evolent. The rotor-eccentric dispenser also contains two parallel rotors. However, in contrast to the plasticator they present themselves parallel rolls with spirally maintained cams. While rotating the cams of one rotor, the other rotor enters into interspaces between the cams. Thus, rotor rotation rate of the combined mixer is 150 r/min. Mixing element of the vertical dispenser consists of a rotating shaft which bears three discs. Both external discs are four blade screws equipped with cams; the latter are bent against each other at a certain angle; an internal disc is a compact one. Rotor rotation rate is 3000 r/min. Clearly the best results are achieved when using the vertical dispenser.

The dependence of the sample texture on the softening point of the used bitumen (i.e., practically on its formulation) is of nonmonotonous nature; the best indices are obtained with bitumen having a softening point of 50°C (Table 3).

As noted above in accordance with the contemporary ideas[1,2] bituminous polymeric compositions represent heterogeneous polydisperse systems, which matrix phase comprises resinous and oil components and a disperse one contains no less than two components—bitumen asphaltenes surrounded by an absorptive layer consisting of the most lyophilic molecules entering into toluene fraction of resins and a dispersed swelled in malthenes polymer. Bitumen parameters, type and concentrate of a polymer entering the composition govern the temperature interval of the material workability (at a stable technology of the ingredients matching).

In this context, when developing optimal bituminous polymeric compositions, consideration must be given to differences in ingredients content, and to the properties of bitumen components. In addition, the latter determine thermodynamic compatibility of bitumen and polymer, BPC homogeneity and service life of the material.[3]

The convenient method of research in polymeric and oligomeric materials is the thermo-mechanical analysis (TMA) whose essence involves making and recording sample deformation ϵ under the influence of the directed external effort which creates some constant (or approximating the constant one) stress δ in a sample. When measuring deformation at constantly changing temperatures T, thermomechanical curve of a material, ϵ (T) is obtained, allowing the determination of transition temperatures between aggregate phase and a relaxation of a polymer. This includes glass transition - softening and flow temperatures, to correlate the levels of sample deformation, to reveal the formation and the breakdown of a space structure, the separation of phases in multicomponent systems, etc. This method evaluates temperature regions of a material workability or, in other words, to determine the so-called "plasticity interval" as the difference in flow and glass transition temperatures. This procedure more adequately complies with the performance properties of the material than the plasticity interval defined as the difference in softening and freezing temperatures.

An investigation of the published data points to the limited TMA application for the study of the bituminous systems. A large amount of papers are dedicated to TMA of bituminous polymeric compositions. The influence of a type, content, molecular weight, molecular weight distribution of a polymer on BPC thermo-mechanical properties have been investigated.[4] On TMA curves of samples with a high elastomer or thermoplastic elastomer content, regions can be reliably detected corresponding to the main relaxation states, and to determine from them glass transition temperature T_g particularly in the case of structure inversion (phase inversion) of a material.

TMA method has been used to investigate the bitumens properties themselves, and their ingredients. The apparatus for studying thermo-mechanical properties of the polymers and dilatometric measurements "UIP-70M" have been used for TMA. Penetration methods have also been used. The chamber-sample holder and a rod with a changeable tip-punch are made of quartz, and the indentor with a diameter of $1.78 \cdot 10^{-3}$m is made of invar. The loading regime is quasi-static, the loads were applied within the range of 0.1 - 6 kPa. The heating rate 2.5°C $min.^{-1}$, the atmosphere is static. A sample heated to the temperature 15-20°C higher than the softening temperature was poured into a dish made of invar, mounted in a sample-holder and cooled with a liquid azote at a constant rate of 2.5°C, $min.^{-1}$ to the temperature −70°C. A cooling rate is equal to a heating rate to avoid fixation of a disbalanced state of a tested sample.

The dilatometric studies of bitumens were carried out with the use of the same apparatus. In this case, the load on a sample accounts for 1-4 Pa.

Bitumen was resolved into fractions (components) in a procedure[5] in the following way. At first, asphaltenes were resolved by hexane extraction in the Sauxlett apparatus. Then malthenes in the form of a solution in isooctane were transferred to silica gel and successively were subjected to dilution by isooctane (in doing so, paraffin naphthenes were giving off PN), to a mixture of isooctane and toluene (9:1) (monocycloaromatic hydrocarbons evolve, MCA), to a mixture of isooctane and toluene (toluene resins, TR) and to a mixture alcohol and toluene (1:1) (alcohol - toluene resins, ATR).

In order to prevent any changes in samples associated with the possible going of the processes of polymerization, oxidation, etc., the samples were kept in desiccator* in darkness at −10°C.

*Desiccator is a glass laboratory vessel provided with the ground stopper in which samples are mounted on a special stand and a tank with sulphuric acid or calcium oxide is placed on its bottom. Exiccator is used for the prevention of absorption by the samples of water vapor, carbon dioxide, etc. from the air.

Figure 6 schematically presents TMA curves of bitumen and its components. As shown in the figure, there is not region of high elasticity for all the samples, and when heating bitumen its components transform directly from a glassy state to a viscous- flow state.

Table 4 presents flow temperatures T_f of bitumen and its components mono- and cycloaromatic fractions and alcohol toluene resins possess the lowest thermal resistance. Relatively high thermal resistance of malthenes is provided by paraffin naphthenes fractions. It is interesting that malthenes flow temperature isn't additive in relation to the similar characteristics of the ingredients resulting from a complex character of bitumen components interaction and/or changing of components properties (and probably composition and structure) due to their partial destruction at release and storage.

Dilatometric curves (TMA curves recorded at loads 4 Pa, Figure 7) differ from the foregoing curves by the presence of dilatometric effect in a low temperature region. This effect is caused by an increase in the specific volume of substances and is connected with the softening (dis-glass transition) of a glassy material.[6] Evidently, temperature of the initial dilatometric effect on TMA curve, called the initial softening temperature, T_{is}, isn't the temperature of structural glass transition. It is likely that the region between the initial softening temperature, T_{is}, and the flow temperature, T_f, is in line with visco-elastic states of bitumen (at certain values of loads and heating rate). In contrast to polymers, it is believed that the mentioned region complies with the most appropriate, from the viewpoint of performance state of bitumen. It is of interest to note the availability of two dilatometric effects on the TMA curve of paraffin - naphthene fractions. The origin of this phenomenon have not been found.

It is anticipated that the research in the TMA region of bitumen combined with the use of other methods of physiochemical analysis (thermal differential analysis, infrared spectroscopy, etc.) will enable the authors to discover a relationship between the plasticity interval and, in the end, the durability of the material with composition and bitumen properties.

CONCLUSIONS

The proposed methods of investigation into bitumens and bituminous-polymeric compositions—qualitative morphological analysis and thermo-mechanical analysis—represent useful instruments which allow the manufacture of composites with predetermined properties by optimization of composition and technology of production mixes.

The application of the mentioned methods creates an opportunity to obtain reliable information on the interrelation between BPC structure and properties.

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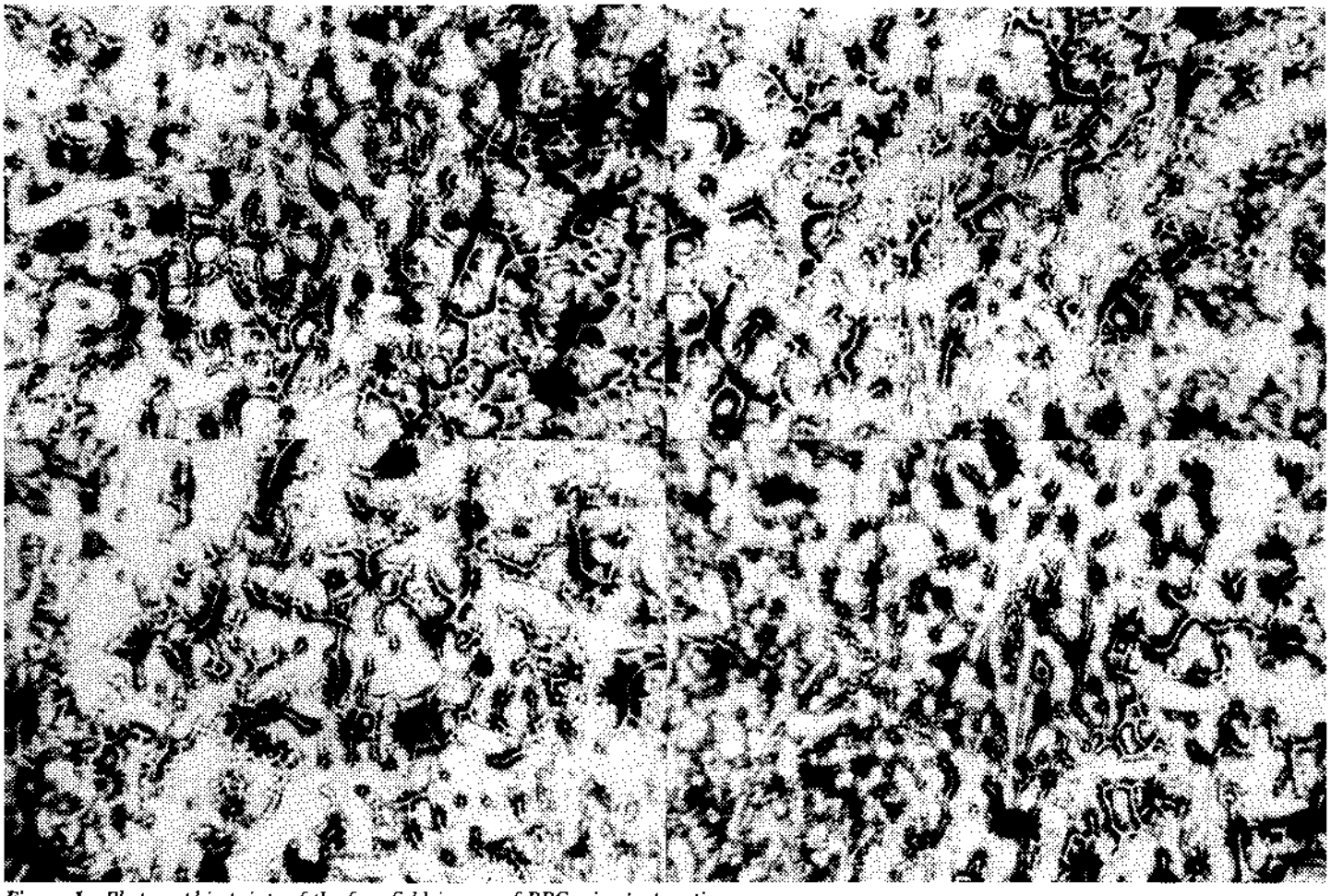

Figure 1 Photographic prints of the four field images of BPC micropreparation.

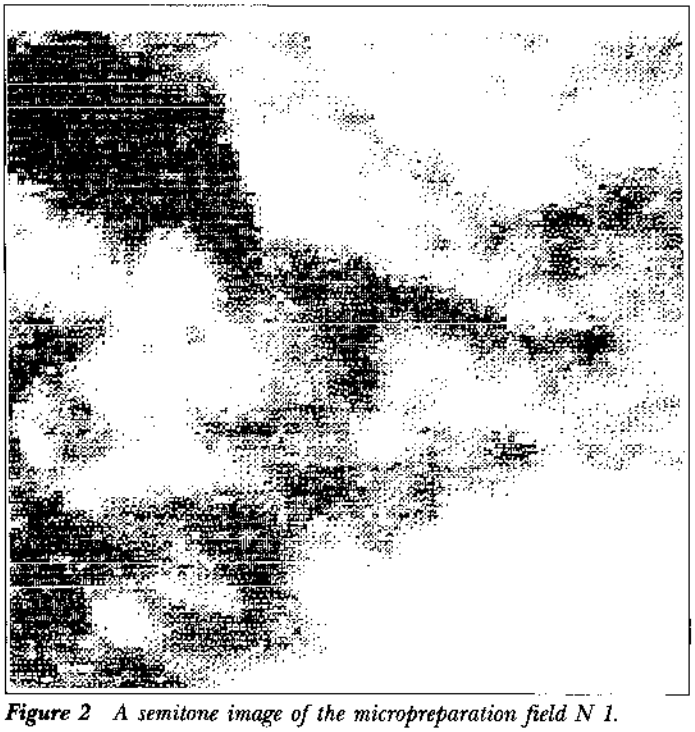

Figure 2 A semitone image of the micropreparation field N 1.

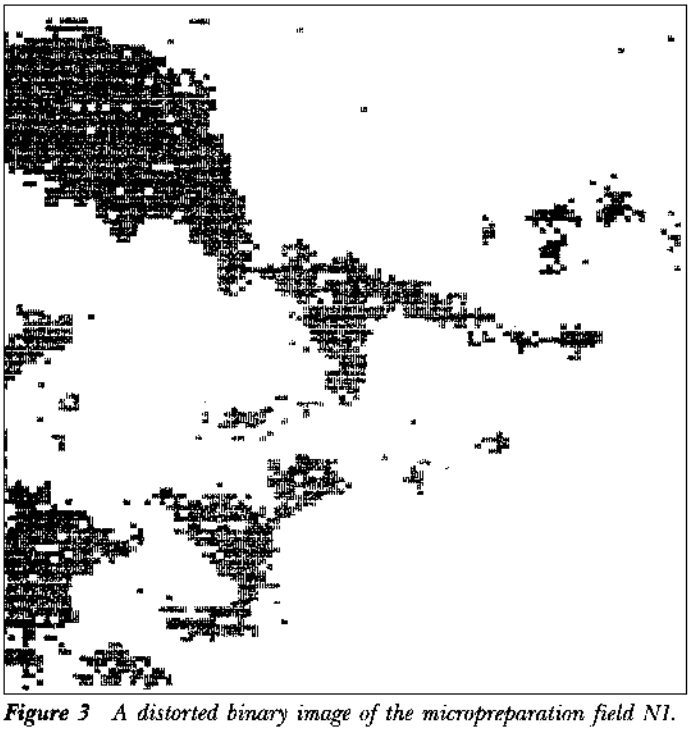

Figure 3 A distorted binary image of the micropreparation field N1.

Figure 4 *Correction of a distorted binary image; a) Results of "distortions removal" operation. b) Results of "packing of pores" operation.*

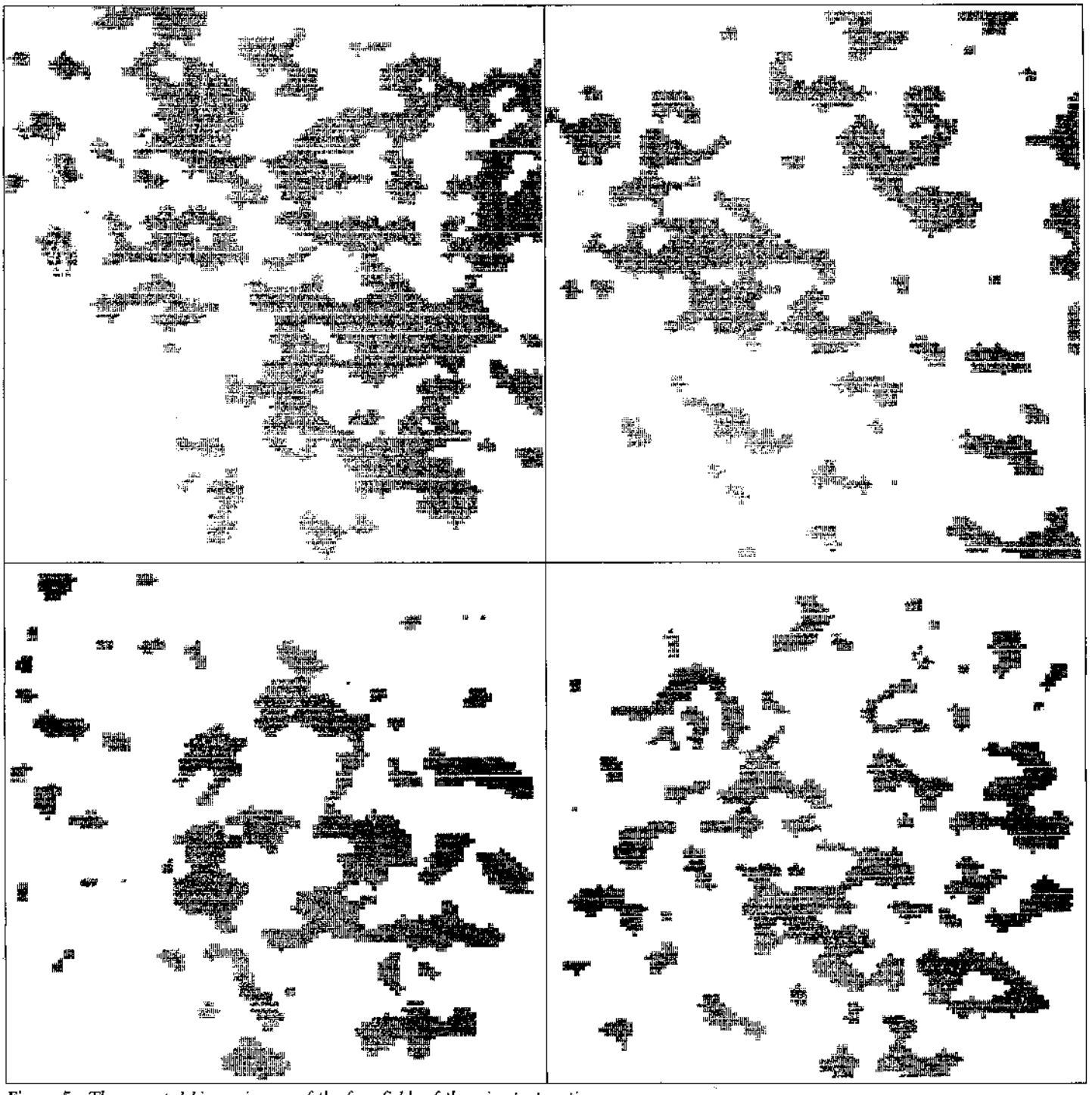

Figure 5 The corrected binary images of the four fields of the micropreparation.

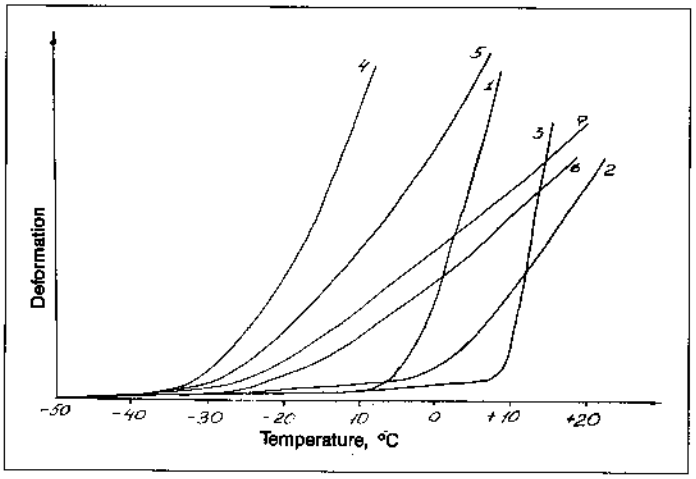

Figure 6 Thermo-mechanical curves of bitumen and its components at load 100 Pa: 1 - bitumen; 2 - malthenes; 3 - PN; 4 - MCA; 5 - BCA; 6 - TR; 7 - ATR.

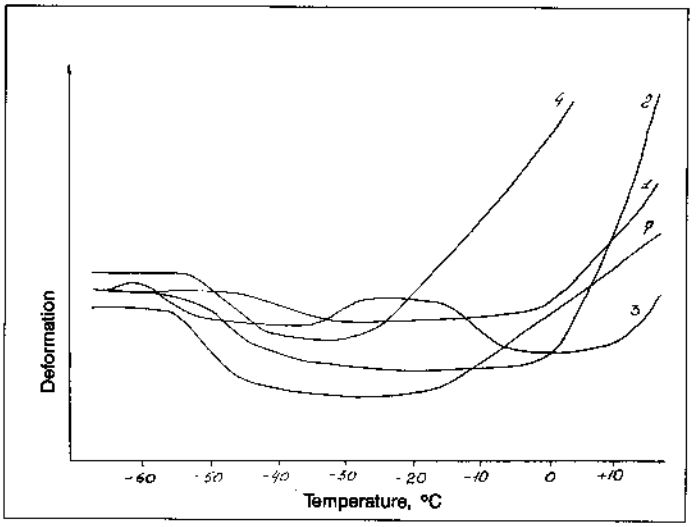

Figure 7 Thermo-mechanical curves of bitumen and its components at load 4 Pa: 1 - bitumen; 2 - malthenes; 3 - PN; 4 - MCA; 5 - BCA; 6 - TR; 7 - ATR.

Mixing time, min.	D_m, mμ	Type of distribution in size	Share of particles with D_m ◄ 56mμ, %	K_m	Composition properties	
					Softening point, (R,B), °C	FRAAS temperature °C
30	64.2	bimodal	61.2	0.72	90	-14
120	57.6	unimodal	68.2	0.57	95	-20
240	51.8	."	78.9	0.32	94	-28

Table 1 The results of the composition study obtained at different duration of mixing (mixer - plasticator).

Mixer type	Mixing time, min.	D_m	Type of distribution	Share of particles with D_m ◄ 56 mμ, %	K_m	Composition properties	
						T_s, °C	T_F, °C
Plasticator	240	57.6	unimodal	68.2	0.57	95	-20
Vertical disperser	240	48.8	unimodal	85.2	0.81	96	-31
Rotor-eccentric dispenser	480	83.4	."	62.3	0.89	63	-20

Table 2 The results of the composition study obtained in the mixers of various types.

T_s	D_m, m	Type of distribution	Share of particles with D_m ◄ 56 mμ	K_m	Composition properties	
					T^s, °C	T^F,°C
42	51.8	unimodal	78.9	0.32	94	-28
50	25.8	."	95.7	0.60	96	-35
62	29.8	."	71.6	0.66	93	-30

Table 3 The results of the composition studies obtained with the use of bitumen blown to different softening points T_s (mixer - plasticator, mixing time 240 min.).

Sample	Components, weight %						T_f, °C
	PN	MCA	BCA	TR	ATR	ASP	
Bitumen	28.2	15.5	4.0	12.4	20.1	19.8	-6
Malthenes	35.2	19.3	5.0	15.4	25.1		0
PN							+8
MCA							-34
BCA							-29
TR							-19
ATR							-29

Table 4 Flow temperatures of bitumen and its components (δ = 100 Pa; bitumen is made of a mixture of West Siberian and Yarega oils, softening temperature 47.5°C, penetration 25°C - 137• 10^{-1}mm, at 0°C - 46• 10^{-1}mm, FRAAS brittleness temperature -29°C.