THERMAL EXPANSION OF BITUMEN-MINERAL COMPOSITIONS

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The article presents the results of investigations of the thermal expansion of bitumen-mineral compositions and their components of different origin, carried out with newly developed dilatometers.

The bitumen-mineral compositions used for road surfacing are a highly concentrated disperse system consisting of mineral filler with a certain grain-size distribution and the medium, bitumen binder. Although thermal expansion of bitumen-mineral compositions is of great practical and scientific importance, it has been investigated much less than, e.g., mechanical strain.

In describing the properties of compositions, we use the "mixture equation," the essence of which in characterizing a certain indicator of a composition P_c is the summing by the volumetric principle of the properties of the components of the composition P_m, P_n, ..., P_i having volumes V_m, V_n, ..., V_i expressed in fractions of unity:

$$P_c = V_m P_m + V_n P_n + \dots + V_i P_i. \tag{1}$$

Bitumen-mineral compositions (usually three-phase composition) consist of the mineral filler, bitumen, and pores. The volume of such a composition V_c then consists of the volume fraction of the mineral filler V_f, of the bitumen V_b, and of the pores V_p:

$$V_c = V_f + V_b + V_p = 1. \tag{2}$$

Upon cooling, the volume of the bituminous binder decreases more than the volume of the filler, and this causes an increase of the volume of the pores in the composition. According to Arand [1], the increase in porosity of bitumen-mineral materials ΔV_p upon cooling is correlated with the thermal compression of the bituminous binder ΔV_b by the relation $\Delta V_p = 0.1\Delta V_b$. If we assume that the porosity of the composition upon cooling changes in the intergranular cavities, then its effect on the thermal expansion of the composition is insignificant, and the system may be viewed as a two-phase system. The thermal coefficient of volume expansion of a composition β_c for a two-phase mixture is determined by the following equation:

$$\beta_c = V_f \beta_f + V_b \beta_b. \tag{3}$$

However, Eq. (3) for a bitumen-mineral composition does not take into account a number of factors affecting thermal expansion: size and distribution, shape, specific surface, and other features of the particles of the mineral filler; interconnection between the surfaces of the phases; thermal stresses in the binder; and also the elastic and viscoelastic properties of the phases. Thus the presented model of the behavior of a bitumen-mineral composition upon change of temperature may differ from reality, though sometimes the linear equation of the mixture is applicable, as, e.g., in the case of natural rubber filled with table-salt particles [2]. There exist a number of equations describing the thermal expansion of compositions with a view to the thermoelastic properties of the phases [2-5]. For compositions with spherical filler Kerner's equation [3] is usually used:

$$\beta_c = V_f \beta_f + V_b \beta_b - (\beta_b - \beta_f) V_b V_f \Theta, \tag{4}$$

where

$$\Theta = \left(\frac{1}{K_b} - \frac{1}{K_f}\right) \Big/ \left(\frac{V_f}{K_b} + \frac{V_b}{K_f} + \frac{3}{4G_b}\right). \tag{5}$$

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Here K_b and K_f are the volumetric moduli of elasticity of the binder and the filler, respectively; G_b is the shear modulus of the binder.

In Kerner's equation, the third term $(\beta_b - \beta_f)V_b V_f \Theta$ characterizes the deviation of β_c from the linear equation for a mixture. It can be seen that in this equation, the effect of the size and surface properties of the filler is not taken into account. However, it is of interest to verify whether this equation is suitable for bitumen-mineral compositions with constant grain-size distribution of the filler.

The object of the present work is to study the thermal expansion of bitumen-mineral compositions with different porosities, mineral fillers, and bitumen binders, and to verify that the above equations are suitable for describing it.

Thermal expansion of bitumen-mineral compositions and of mineral materials was studied with an automatic linear dilatometer [6], and that of bitumen binders with a volume dilatometer [7]. The objects of investigation were bitumen-mineral compositions with bitumen binders: of low viscosity with structure sol—gel (specimen No. 1), and also of high viscosity with a structure close to sol (specimen No. 2), having the structure sol—gel and gel—sol (specimens Nos. 3 and 4, respectively), and with a structure close to gel (specimen No. 5, Table 1). The specimens of bitumen-mineral compositions were studied with limestone and granite filler.

The results of the dilatometric tests of bitumen-mineral compositions made with limestone mineral filler of granulometry type "G" according to GOST 9128-76 with optimum content of 0.14 volumetric part of bitumen binder brand END 90/130 (specimen No. 4), and separately of limestone and bitumen, are shown in Fig. 1. It can be seen from the dilatogram for limestone that at temperatures between +50 and —70°C its linear thermal expansion coefficient (LTEC) is constant and equal to $0.5 \cdot 10^{-5}\,{}^\circ C^{-1}$. Thermal expansion of the bitumen binder above and below its glass-transition temperature T_g^b, which for specimen No. 4 was equal to —33°C, is characterized by the values of LTEC $20.7 \cdot 10^{-5}$ and $10 \cdot 10^{-5}\,{}^\circ C^{-1}$, respectively.

In bitumen-mineral composition, the thermal expansion determined experimentally and calculated by Eq. (3) differs both in the nature of its dependence on the temperature and in magnitude (Tables 1 and 2). At temperatures above T_g^b, the thermal deformations of the bituminous binder and the mineral filler change linearly, whereas that of the bitumen-mineral composition varies according to a curvilinear dependence.

At temperatures between 10 and 25°C, a structural transition occurs in the compositions which we call the fluidity temperature T_F^c. This transition can be seen more distinctly when the specimen is being heated (Fig. 1). At temperature above T_F^c, the LTEC of a bitumen-mineral composition α_{1e} is smaller than at temperatures below T_F^c, i.e., α_{2e}; its anomalous change at elevated temperature is due to the peculiarities of deformation of the bituminous binder in the composition.

The bituminous binder, which is amorphous at the operating temperatures, is in a state of thermodynamic unbalance. The degree of deviation from the equilibrium state of the bitumen structure in the composition is much greater than in the free state. With further cooling due to loss of mobility of the new components, the structure of the bitumen becomes more unbalanced. At the same time, with decreasing temperature and the possibility appearing of an approach of the high-molecular-weight structural elements that have lost their mobility at higher temperatures, ordered microstructures may form and bonds be established that are not ruptured even upon heating to temperatures exceeding T_F^c. Such equilibrium structures, formed by the high-molecular-weight components of the bitumen, are denser than the disordered unbalanced structure and ensure greater strength of the contact filler—binder—filler. This manifests itself in increased compressive strength at 50°C of specimens of bitumen-mineral compositions subjected to thermal cycling in the temperature interval +30 to —16°C (Fig. 2). A decrease in the LTEC α_{1e} of the composition at temperatures above T_F^c (Fig. 1, Table 2) is caused by the flow of unbound bitumen binder into the pores of the composition, and this is confirmed by the decrease in porosity of the composition during the process of thermal cycling (Fig. 2).

The second structural transition in the bitumen-mineral composition is associated with the glass transition of the bituminous binder. It follows from Fig. 1 that the glass-transition temperature of the bitumen-mineral composition T_g^c is 5°C lower than the glass-transition temperature of bitumen T_g^b (specimen No. 4). It would seem that T_g^c has to be higher than T_g^b because of the limitation of molecular mobility of the material of the bituminous binder adsorbed on the surface of the mineral material. However, on the surface of the mineral binder, the most highly polar components of the bitumen are adsorbed, i.e., asphaltenes and part of the tars, which, as is well known [8], have little effect on T_g^b. The binding of the polar components of the bitumen on the surface of the mineral filler reduces the action of the orienting and induction intermolecular forces among the molecules of the hydrocarbon components of the binder, and, as a result, T_g^c decreases and the glass-transition temperature interval of the bitumen as part of the bitumen-mineral composition broadens. It can be seen from Fig. 1 that the difference $T_2^c - T_1^c$ in the composition based on bitumen No. 4 is 33°C, which is 14°C larger than the glass-transition interval of free bitumen.

Thermal expansion of bitumen-mineral compositions is directly associated with the thermal expansion of bitumen when the other parameters are equal (Tables 1 and 2). The composition based on low-viscosity bitumen No. 1 has a higher LTEC than the composition based on high-viscosity bitumen No. 3 of the same rheological type. This is in agreement with the theory of free volume of liquids and amorphous bodies, according to which less-viscous liquids, having greater molecular mobility and correspondingly larger free volume, have a higher LTEC than highly viscous liquids [9]. A decrease in the LTEC is also a characteristic feature of polymers with increasing degree of their polymerization and increasing viscosity [10]. When the structure of bitumen in the composition changes from sol to sol—gel, the LTEC decreases (bitumens Nos. 2, 3, 4 in Table 2), and upon transition to gel (specimen No. 5) it increases again. The T_g^c is 3-7°C lower than the T_g^b, and this difference increases as the structure of the bitumen changes from sol to gel (Tables 1 and 2). The T_F^c in bitumen-mineral compositions does not depend much on the rheological type and the viscosity of the bitumen (Table 2); in thermal cycling T_F^c is shifted to the side of the higher values (Fig. 2).

The values of LTEC of bitumen-mineral compositions determined experimentally, α_e, and with the aid of calculations by the equation for the mixture (3), α_t^M, and Kerner's equation (4), α_t^c, were compared by substituting the experimentally found parameters for the components of the composition: $V_f = 0.82$; $\beta_f = 3\alpha_f = 1.5 \cdot 10^{-5}\,°C^{-1}$; $V_b = 0.14$; and β_b from Table 1.

As was to be expected, the experimentally determined values of LTEC for bitumen-mineral compositions are lower than those found by the equation for the mixture. In the temperature interval T_g^c-T_F^c the LTECs of the bitumen-mineral mixture α_{2e} and α_{2t}^M differ less than α_{3e} and α_{3t}^M at temperatures below T_g^c; this may be due to the lesser limitation of deformation of the bituminous binder by the surface of the filler at temperatures above T_g^c and the lower thermal stresses in it. Between the LTECs determined experimentally and theoretically by Eq. (3) for a bitumen-mineral composition based on limestone of granulometry type "G" (GOST 9128-76) there is the following correlation:

$$\alpha_{2e} = 0.85\,\alpha_{2t}^M, \tag{6}$$

$$\alpha_{3e} = 0,73\,\alpha_{3t}^M. \tag{7}$$

These correlations are practically not affected by the porosity of the composition. It was experimentally established that when porosity changes from 0.07 to 0.02 of the volume of the composition due to the different degree of compaction, the values of LTEC differ by 2.9%, which lies within the limits of the experimental error.

Equations (6) and (7) describe satisfactorily the relation between the theoretical and the experimental values of LTEC, not only for compositions with optimum binder content, but also for compositions with binder content other than optimal. For instance, for bitumen-mineral compositions with filler content from 0.90 to 0.75 volume parts, the experimental and theoretical values of LTEC are described perfectly satisfactorily by Eqs. (6) and (7) (Fig. 3).

There are no anomalies in the dependences (Fig. 3) of the experimental values of LTEC of the compositions if the content of filler is very large, when the bitumen film, according to [11, 12], may attain a thickness of 5-10 μm and be in the adsorbed state, or if the filler content is moderate and most of the bitumen is situated in the interpore space. This may

TABLE 1. Origin and Properties of Bitumens from the Residues of Ramashkin Petroleum

No. of bitumen	Technology of obtaining bitumen	Depth of penetration of needle, 0.1 mm at 25°C	Temp., °C		Thermal coeff. of vol. expansion $\beta\cdot10^{-4}$, °C at temps.		Brand of bitumen
			of softening T_{soft}	of glass transition T_g^b	above T_g^b	below T_g^b	
1	Vacuum concn.	202	40,5	—32,5	6,45	3,20	BN 130/200
2	Compounding of deasphaltization asphalt with extract IV fr. (93 : 7%)	106	43	—28	6,10	3,00	BN 90/130
3	Vacuum concentration	106	44	—31	5,90	2,90	BN 90/130
4	Oxidation in a still of asphalt with nominal viscosity at 80°C-82 sec	104	46	—36	6,20	3,00	BND 90/130
5	Compounding of asphalt of propane deasphaltization oxidized to T_{soft} 120°C with extract IV fr. (55 : 45%)	102	48	—35	6,50	3,40	BND 90/130

TABLE 2. Dilatometric Characteristics of Bitumen-Mineral Compositions

No. of bitumen in composition	Glass-transition temp. T_g^c, °C	Temp. of fluidity T_F^c, °C	Linear thermal expansion coeff. LTEC $\cdot10^{-5}$, °C^{-1}						$k_1=\frac{\alpha_{1e}}{\alpha_{1t}^M}$	$k_2=\frac{\alpha_{2e}}{\alpha_{2t}^M}$	$k_3=\frac{\alpha_{3e}}{\alpha_{3t}^M}$
			exp.			calc. by (3)					
			α_{1e}	α_{2e}	α_{3e}	α_{1t}^M	α_{2t}^M	α_{3t}^M			
Mineral filler: limestone											
1	—36	+15	0,90	2,96	1,40	3,42	3,42	1,90	0,26	0,86	0,74
2	—32	+15	1,04	2,79	1,30	3,26	3,26	1,81	0,32	0,85	0,72
3	—35	+14	1,12	2,69	1,29	3,16	3,16	1,76	0,35	0,85	0,73
4	—38	+14	1,28	2,80	1,30	3,31	3,31	1,81	0,39	0,85	0,72
5	—42	+15	1,42	2,88	1,37	3,45	3,45	2,00	0,41	0,84	0,69
Mineral filler: granite											
3	—34	+12	0,86	2,60	1,26	3,12	3,12	1,72	0,27	0,83	0,73
4	—38	+14	1,02	2,78	1,25	3,27	3,27	1,77	0,31	0,85	0,71

indicate that the decrease in thermal expansion of the bituminous binder, situated in the composition, at temperatures below T_F^c is determined chiefly by the limiting action of the filler surface on the deformability of the bitumen.

In finding the LTEC of bitumen-mineral compositions by Kerner's equation, there are difficulties connected with the complexity of the experimental determination of K and G of the bituminous binder. These parameters were therefore taken from [13] for a bituminous binder that is of analogous origin and brand as specimen No. 3. If we substitute into (4) the values $V_b = 0.14$; $\beta_{2b} = 59\cdot10^{-5}$ and $\beta_{3b} = 29\cdot10^{-5}\,°C^{-1}$; $V_f = 0.82$; $\beta_f = 1.5\cdot10^{-5}\,°C^{-1}$; $K_b = 2.7\cdot10^9$ N/m^2; $G_b = 1.24\cdot10^9$ N/m^2; $K_f = 4.86\cdot10^{10}$ N/m^2, we find from $\alpha = \beta/3$ the LTECs of the composition α_{2t}^c and α_{3t}^c, which were equal to $2.32\cdot10^{-5}$ and $1.35\cdot10^{-5}\,°C^{-1}$, respectively. The relations between $\alpha_{2e}/\alpha_{2t}^c$ and $\alpha_{3t}/\alpha_{3t}^c$, determined experimentally and by Kerner's equation, show that at temperatures above T_g^c, the LTEC found by Kerner's equation α_{2t}^c is smaller than the experimental value α_{2e}, while at temperatures below T_g^c, the LTEC α_{3t}^c is approximately equal to α_{3e}. The reason for this may be that Kerner's equation does not take the relaxation of thermal stresses in the binder into account at temperatures above T_g^c, and this in the final analysis leads to higher values of LTEC when they are experimentally determined.

It follows from the above that the two-phase model of bitumen-mineral compositions is well described by equation of mixture upon introduction of the coefficients k_2 and k_3, taking into account the limitation of the deformability of bitumen by the surface of the mineral

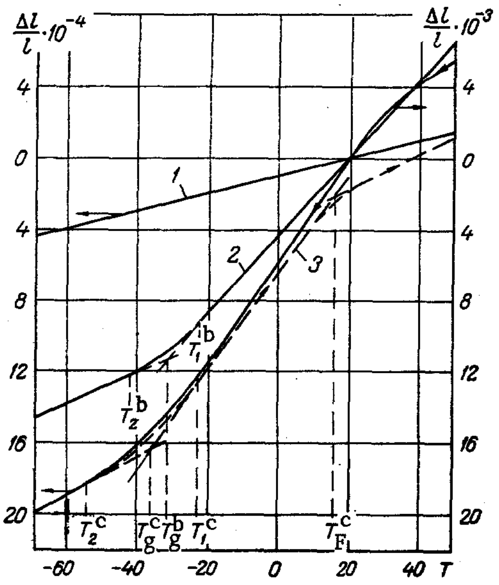

Fig. 1

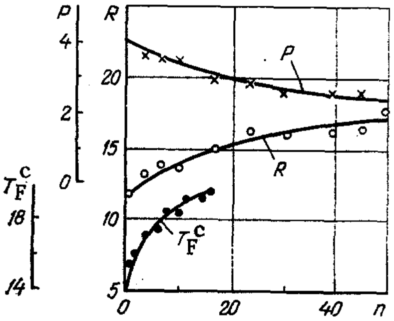

Fig. 2

Fig. 1. Dilatogram of mineral filler, viz., limestone (1), of bitumen binder, specimen No. 4 (2), and of bitumen-mineral composition (3).

Fig. 2. Change in strength R(N/m^2) at 50°C, porosity P (volume fraction), and of fluidity temperature T_F^c (°C) in thermal cycling of specimens of bitumen-mineral composition from +30 to −16°C.

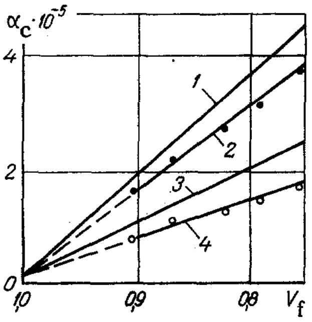

Fig. 3. Dependence of the coefficients of thermal expansion of the compositions on the filler content: 1) α_{2t}^M calculated; 2) α_{2e} experimental; 3) α_{3t}^M calculated; 4) α_{3e} experimental. $\alpha_c \cdot 10^{-5}$, °C^{-1}.

filler compared with the deformability of free binder. It can be seen from Table 2 that the coefficients k_2 and k_3 do not depend on the brand and origin of the bitumens, and that they remain unchanged in compositions with limestone or granite mineral fillers (Table 2).

Thus the above model and Eqs. (3), (6), and (7) characterize sufficiently objectively the mechanism of thermal expansion of bitumen-mineral compositions in the viscoelastic and elastic states, and they describe satisfactorily the dependence of the LTEC of compositions on the properties and ratios of their components.

NOTATION

P_c, index of the property of the composition; P_m, P_n, P_i, indices of the properties of the components of the composition; V_m, V_n, V_i, volumes of the components of the compositions; V_c, volume of the composition; V_f, volume of the filler; V_b, volume of the bituminous binder; V_p, volume of pores; β_c, β_f, β_b, thermal coefficients of volume expansion of composition, filler, and bituminous binder, respectively; K_b, K_f, volumetric moduli of elasticity of bituminous binder and filler, respectively; G_b, shear modulus of bituminous binder; T_g^b, T_g^c, glass-transition temperatures of bituminous binder and composition, respectively; T_1^b, T_2^b, temperatures of beginning and end of the glass transition of bitumen, respectively; T_1^c, T_2^c, temperatures of beginning and end of the glass transition of composition, respectively; T_F^c, fluidity temperature of the composition; α_f, α_b, linear thermal expansion coefficients of filler and bituminous binder, respectively; α_{1e}, α_{2e}, α_{3e}, linear thermal expansion coefficients of composition at temperatures above T_F^c, in the interval T_F^c-T_g^c, and below T_g^c, respectively, found experimentally; α_{1t}^M, α_{2t}^M, α_{3t}^M, the same, found theoretically by the equation for a mixture; α_{1t}^c, α_{2t}^c, α_{3t}^c, the same, found theoretically by Kerner's equation; k_2, k_3, coefficients taking into account the effect of the filler surface on the thermal expansion of the bituminous binder in the temperature interval T_F^c-T_g^c and below T_g^c, respectively.

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