DOI 10.1007/s10553-018-0895-x
*Chemistry and Technology of Fuels and Oils, Vol. 54, No. 1, March,2018 (Russian Original No.1, January – February, 2018)*

## RESEARCH

# STRUCTURAL AND MECHANICAL PROPERTIES OF PARAFFIN WAX COMPOSITES

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*The deformation-strength (strength and plasticity) and dilatometric (contraction or volume shrinkage) properties of binary composites of solid edible paraffin wax P-1 with ceresins C-65, C-80, and C-85, waxes, and soft paraffin waxes are studied. Diagrams of propertycomposition state are constructed. The functional dependencies of these properties on the content of modifying components in the composites with paraffin wax P-1 are established.*
***Keywords:*** *petroleum paraffin, ceresin, wax, composite blends, composition, strength, plasticity, volume shrinkage.*

In many branches of the industry (chemical, radioelectronic, engineering, food, packaging, etc.), where solid paraffin waxes and their melts with ceresins and waxes are used, their equivalent substitute has not been found so far. The demand for paraffinic petroleum products continues to rise alongside increasing shortage of petroleum paraffin wax containing materials. Wide use of these petroleum products stems from their unique properties, such as temperature (temperatures of melting and hexagonal-rhombic H→R phase conversions in solid state) and structural-mechanical (strength, volume shrinkage or contraction, plasticity, etc.).

Depending on the area of application, each of which places specific demands on the quality of the used paraffin melts, they must have the requisite set of performance properties resulting from their composition

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and crystalline disperse structure. The main goal of this study was, therefore, to decipher the nature of the influence of the composition of the paraffin composites on their structural-mechanical properties.

Considering that the structural-mechanical properties of paraffins and ceresins differ considerably [1], we studied the pattern and peculiarities of change of these properties upon compounding of paraffinic petroleum products with each other. It was shown in [2-7] that several performance properties (including physicomechanical) of the paraffins could be changed by adding ceresins and polymeric materials to the paraffins. Some compositions of paraffin-wax composites for food and agricultural branches of the national economy are given in patents [8-11]. These works of practical importance, however, are of a fragmentary nature.

In preparing paraffin composites, edible paraffin of P-1 brand, which was compounded with soft paraffins, waxes, and ceresins, was used as the base. The following petroleum products were used to produce binary mixtures with P-1 paraffin: test samples of soft paraffins waxes of Ozek-Suat (MP-1) and Romashkino (MP-2) crude oils, commercial samples of C-65, C-80, and C-85 ceresins from the Volgograd refinery, and ZV-1 protective wax from the Yaroslavl refinery. The chemical composition and physicochemical properties of these petroleum products are cited in [1].

Note that soft petroleum paraffins have light fractional composition with prevalence of $n$-$C_{21}H_{44}$ – $n$-$C_{23}H_{48}$ fractions (concentration of each of these hydrocarbons is 11-13 wt. %), contain 60 wt. % $n$-alkanes and occur in highly plastic (soft) hexagonal α-phase at room temperature. The P-1 paraffin-ceresin-petroleum wax composites were prepared by their combined fusion at temperatures 20 degree higher than the crystallization temperature of higher-melting products. The strength at 293 K temperature ( $P_m^{293}$ ), volume shrinkage (contraction) in the temperature range from crystallization

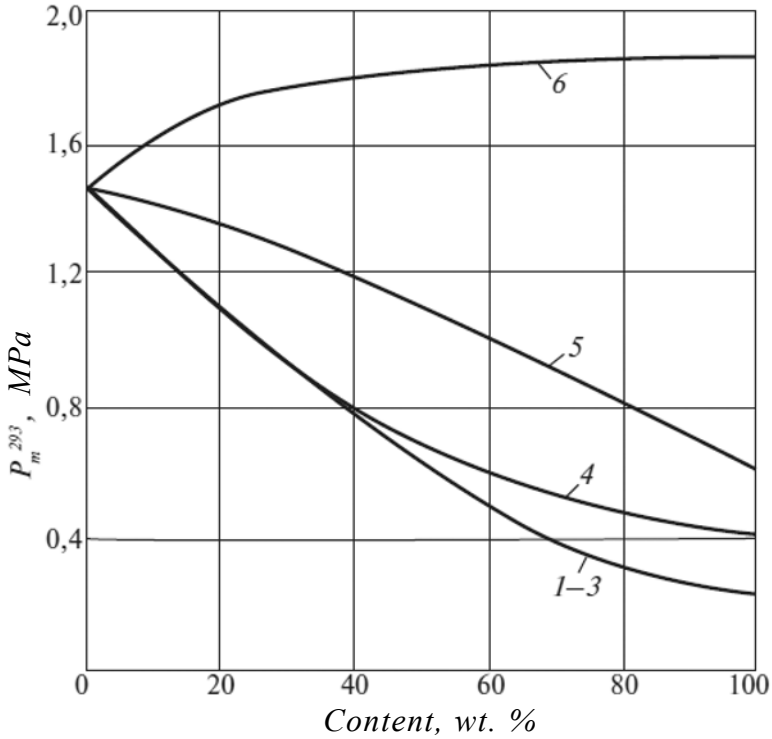


Fig. 1. Dependence of strength ( $P_m^{293}$ ) of disperse structures of binary melts of P-1 solid paraffin with ceresins, waxes, and soft paraffins on their content: 1 MP-1, 2 MP-2, 3 C-65, 4 ZV-1, 5 C-80, and 6 C-85.

initiation to 293 K ( $\Delta V_{T_s}^{293}$ ), and plasticity properties at 293 K ( $\varepsilon_m / P_m$ ) were measured on a specially built laboratory unit, whose design features and the procedure of investigations on which are described in [1].

The dependencies of the strength $P_m^{293}$, plasticity $\varepsilon_m / P_m$, and contraction $\Delta V_{T_s}^{293}$ of binary paraffin and paraffin-wax melts on the composition are shown in Figures 1-3 as diagrams of propertycomposition state.

As can be seen from Fig. 1, compounding of solid paraffin with other paraffin-containing petroleum products facilitates reduction of strength $P_m^{293}$ of disperse structure of the obtained melts provided the added product has a strength index lower than that of the paraffin itself and vice versa. In this context, samples of soft paraffins MP-1 and MP-2, ceresin C-65, and protective wax ZV-1, which have very close low $P_m^{293}$ values (0.2-0.4 MPa), reduce $P_m^{293}$ of melts almost equally in the whole range of change in their concentration from 1 to 99% (Fig. 1,curves 1-4). The strength of melts of only one of the studied petroleum products, namely, C-85 ceresin whose $P_m^{293}$ is higher than that of P-1 solid paraffin by 0.35 MPa ( $P_m^{293}$ of C-85 = 1.85 MPa), increases. The pattern of change in $P_m^{293}$ value of P-1 in melts with C-85 is akin to the dependence of their melting temperature Ts on the composition shown by us in [12]. This points to the dominant role of high-molecular-weight long-chain n-alkanes C-85 as the strength carriers in the formation of the disperse structure of its melts with paraffin. In all other cases, very imperfect disordered crystalline structure of ceresins and waxes containing more than a half of iso- and cyclohexanes [1] as well as a very wide range of homologs of n-alkanes weakens the melts. So, the studied modifiers of the

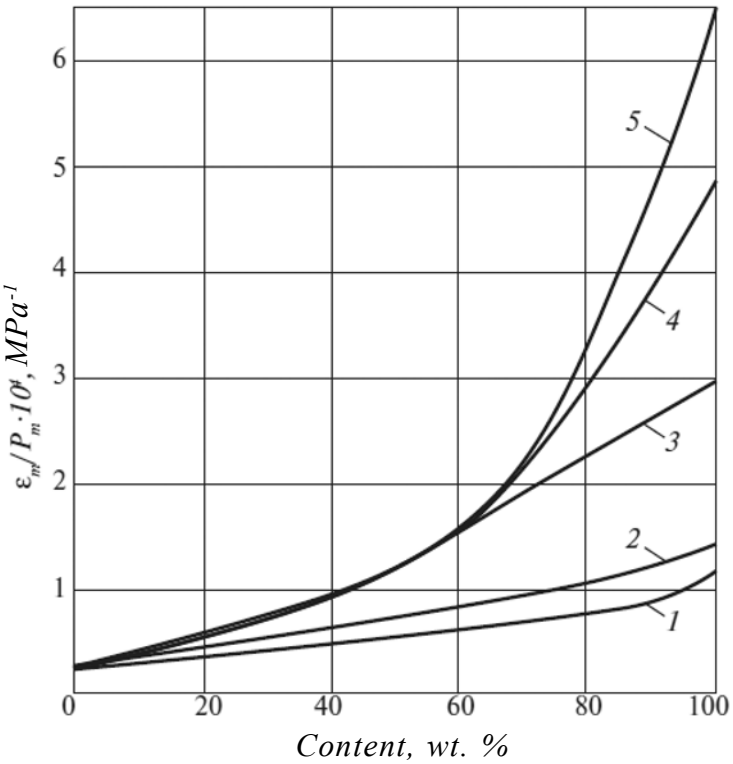


Fig. 2. Dependence of plasticity ( $\varepsilon_m / P_m$ ) of disperse structures of binary melts of solid P-1 solid paraffin with ceresins, waxes, and soft paraffins on their content: 1 C-80, 2 ZV-1, 3 C-65, 4 MP-2, and 5 MP-1.

disperse structure of P-1 solid paraffin can be tentatively divided into two groups, namely, strengthening and destructing agents. The first group includes ceresin C-85 ( $P_m^{293}$ = 1.85 MPa). The second group includes ceresin C-80 ( $P_m^{293}$ = 0.60 MPa), ceresin C-65 (0.4 MPa), ZV-1 (0.25 MPa), and soft paraffins MP (0.2 MPa).

It was important to compare the experimental data on the strength of disperse structure $P_m^{293}$ of paraffins and ceresins with their hardness, which can be estimated from the depth of needle penetration into the product at 293 K. Thus, for petroleum paraffins having strengths in the 0.8-1.4 MPa range, penetration is 32-13 × $10^{-4}$ m. For petroleum ceresins with $P_m^{293}$ = 0.2-0.6 MPa, penetration varies in the 28-16 × 10-4 m range, i.e., with a much lower (2-4 times) strength, ceresins have penetration and, consequently, hardness in almost the same range as do the paraffins. Hence it follows that the depth of penetration, which is so far the only physicomechanical index of quality of petroleum paraffin products fixed by GOST, does not always unambiguously correlate with the strength and therefore cannot replace the latter for evaluating the characteristics of the crystalline structure and the forces of intermolecular interactions that determine it. The needle penetration depth in a paraffin characterizes to a certain measure the propensity of its crystalline structure to plastic deformations. Penetration is greater, the softer and more plastic the crystals and less dense their packing are. Ceresins consisting of hydrocarbons with a higher molecular weight than paraffins have a finer disperse crystalline structure with a greater crystal packing density. In this case, the fine lamellate crystals of ceresins consisting of a larger number of lamellae should be less amenable to needle penetration (deformations) than larger lamellate paraffin crystals with a smaller number of lamellae, which indeed is noticed in practice.

The change in the degree of plasticity of the disperse structure of paraffin composites with ceresins and waxes as a function of their composition is shown in Fig. 2. Ceresins and waxes, as evident from Fig. 2, are

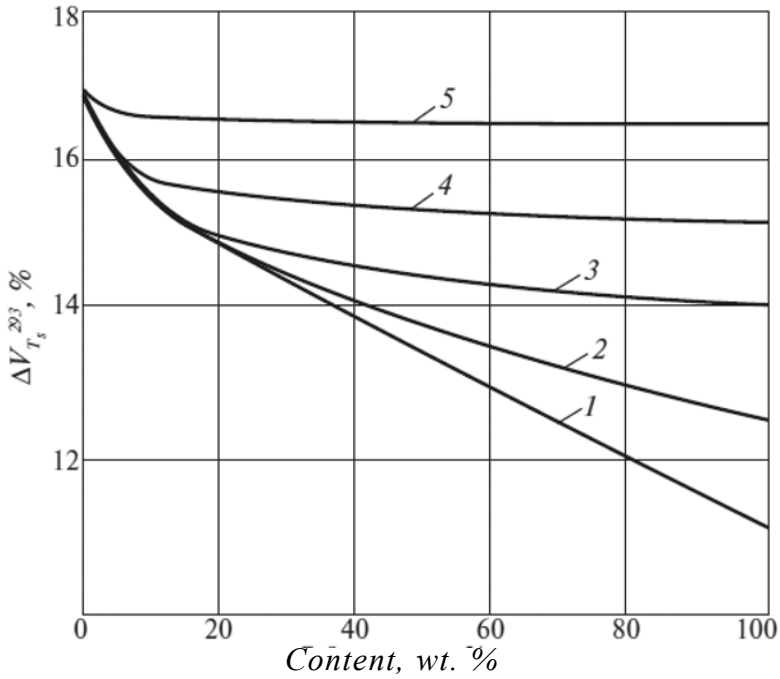


Fig. 3. Dependence of volume shrinkage (contraction) of disperse structures of binary melts ( $\Delta V_{T_s}^{293}$ ) of P-1 solid paraffin with ceresins, waxes, and soft paraffins on their content: 1 MP-1, 2 MP-2, 3 C-65, 4 ZV-1, and 5 C-80.

Table 1

| Functional dependencies | Range of wax, ceresin, and soft paraffin contents in composites for which the dependence is valid | Possible maximum relative error, % |
|---|---|---|
| $P_m^{293}$ = 14.30 - 0.34 with (ZV -1) | 0 < with (ZV -1) < 20 | 3.2 |
| $P_m^{293}$ = 11.19 - 0.07 with (ZV -1) | 20 < with (ZV -1) <100 | 4.9 |
| $P_m^{293}$ = 14.49 - 0.15 with ( C-65) | 0 < with (C-65) < 60 | 5.0 |
| $P_m^{293}$ = 9.77 - 0.08 with (C-65) | 60 < with (C-65) < 100 | 6.0 |
| $P_m^{293}$ = 14.57 - 0.03 with (C-80) | 0 < with (C-80) < 40 | 0.2 |
| $P_m^{293}$ = 15.75 - 0.09 with (C-80) | 40 < with (C-80) < 100 | 3.0 |
| $P_m^{293}$ = 15.16 - 0.09 with (C-80) | 0 < with (C-80) <100 | 4.0 |
| $P_m^{293}$ = 14.14 - 0.18 with (C-65. ZV -1) | 0 < with ( C-65, ZV -1) <20 | 5.0 |
| $\Delta V_{Ts}^{293}$ = 15.49 - 0.03 with (MP-1) | 0 < with (MP -1) <100 | 1.0 |
| $\Delta V_{Ts}^{293}$ = 15.88 - 0.047 with (MP-2) | 0 < with (MP -2) <100 | 1.0 |
| $\Delta V_{Ts}^{293}$ = 14.94 - 0.01 with (ZV -1) | 0 < with (ZV -1) <100 | 0.3 |
| $\Delta V_{Ts}^{293}$ = 15.86 - 0.009 with (C-65) | 0 < with (C-67) < 100 | 0.4 |
| $\Delta V_{Ts}^{293}$ = 16.5 + 0.00042 with (C-80) | 0 < with (C-80) <100 | 0.1 |
| $\varepsilon_m / P_m$ = 0.24 + 0.025 with (MP -1) | 0 < with (MP -1) < 60 | 5.0 |
| $\varepsilon_m / P_m$ = 0.26 + 0.020 with (MP -2) | 0 < with c (MP -2) < 60 | 4.0 |
| $\varepsilon_m / P_m$ = 0.37 + 0.008 with (ZV -1) | 0 < with (ZV -1) < 60 | 2.0 |
| $\varepsilon_m / P_m$ = 0.27 + 0.018 with (C-65) | 0 < with (C-65) < 60 | 4.0 |
| $\varepsilon_m / P_m$ = 0.36 + 0.0057 with (C-80) | 0 < with (C-80) < 60 | 4.0 |

Table 2

| Functional dependencies | Possible maximum relative error, % |
|---|---|
| $\left(P_m^{293}\right)_{pc} = 10.81 - 0.09\, c_w + 0.58 \left(P_m^{293}\right)_w$ | 9 |
| $\left(\Delta V_{T_s}^{293}\right)_{pc} = 9.29 - 0.029\, c_w + 0{,}51 \left(\Delta V_{T_s}^{293}\right)_w$ | 3 |
| $\left(\varepsilon_m P_m\right)_{pc} = 0.021\, c_w + 0.14 \left(\varepsilon_m P_m\right)_w - 0{,}24$ | 10 |

Note. The subscripts *pc* and *w* denote paraffin composite and wax, respectively.

plasticizers of disperse paraffin structure, which enhance plasticity of paraffin composites. In terms of degree of diminution of plasticizing effect on solid paraffins, which is estimated by the quantity em/Pm, the studied petroleum modifiers of disperse paraffin structure lie in the following order: soft paraffins MP-1, MP-2, ceresin C-65, wax ZV-1, and ceresin C-80.

The contractioncomposition correlation for the studied paraffin composites is shown in Fig. 3.

As evident from Fig. 3, petroleum modifiers reduce contraction (volume shrinkage) of paraffin melts, most significantly at concentrations up to 10-20 wt. %. This indicates disordering effect of modifiers on the crystalline structure of the paraffin.

Using the obtained experimental data on the change in $P_m^{293}$, $\Delta V_{Ts}^{293}$, and $\varepsilon_m / P_m$ of P-1 solid paraffin, which occurs due to compounding of the latter with ceresins, waxes, and soft paraffins, and employing computer-aided stepwise multiple regression method, we established the mathematical dependencies of these properties on the content of the modifying component in the composites with P-1 paraffin (Table 1).

The formulas in Table 1 can be used to calculate the values of the respective structural-mechanical properties, such as strength $P_m^{293}$, plasticity $\varepsilon_m / P_m$, and contraction $\Delta V_{Ts}^{293}$ 3 of binary composites of P-1 solid paraffin with the other studied paraffinic petroleum products at fixed contents of the latter as well as the requisite composite composition that ensures their assigned properties.

The calculating functional dependencies shown in Table 2 are recommended for practical use, regardless of the properties of the original solid paraffin and specific brand of the added petroleum wax component. The content range of the studied petroleum wax modifiers, for which the dependencies shown in shown in Table 2 are valid, is $0 < c_w \leq 90\%$.

Using these mathematical correlations, we can calculate how much of the wax component having known properties ($P_m^{293}$, $\varepsilon_m / P_m$, and $\Delta V_{Ts}^{293}$) needs to be added to any solid petroleum paraffin to get a composite with the set value of the respective performance quality index.

Based on the investigation results, the following conclusions can be drawn:

1. The studied samples of commercial petroleum paraffins, ceresins, and waxes in the order of increase in strength of their disperse structure $P_m^{293}$ from 0.13 to 1.8 MPa and concentration $\Delta V_{Ts}^{293}$ from 11 to 17% and decrease in plasticity $\varepsilon_m / P_m$ from 6.5 to 0.4×10-4 MPa-1 lie in the following sequence: soft paraffin, ceresin C-65, wax ZV-1, ceresin C-80, solid paraffin P-1, and ceresin C-85.

2. It is shown by diagrams of property-composition state of binary paraffin composites that compounding of paraffin P-1 with other petroleum products facilitates diminution of $P_m^{293}$ and $\Delta V_{Ts}^{293}$ values of the disperse structure of the obtained melts provided the added components have values of these parameters that are lower than those of paraffin and vice versa. All the studied modifiers weakened and plasticized the structure of P-1 except for C-85 ($P_m^{293}$ = 1.85 MPa) which is a strengthening agent.

3. Computer-aided stepwise multiple regression method was employed to get mathematical relationships that can be used to evaluate the performance properties $P_m^{293}$, $\Delta V_{Ts}^{293}$, and $\varepsilon_m / P_m$ of paraffin composites of various compositions with a precision of not less than 95% and to determine at which qualitative and quantitative content of the modifying components in the composites the set values of these properties could be obtained.

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