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# PRODUCTION OF BITUMEN MODIFIED WITH LOW-MOLECULAR ORGANIC COMPOUNDS FROM PETROLEUM RESIDUES. 8. PROSPECTS OF USING FORMALDEHYDE MODIFIED TARS IN ROAD CONSTRUCTION

***Volodymyr Gunka[1], Myroslava Donchenko[1], Yuriy Demchuk[1,2, ✉], Iryna Drapak[2], Michael Bratychak[1]***

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**Abstract.** Modification of tars with formalin (37 % aqueous solution of formaldehyde) was carried out using various acids as process catalysts with the aim of obtaining new binding materials for road construction. $H_2SO_4$, HCl, $H_3PO_4$, and $CH_3COOH$ were used as catalysts. The modification process was carried out in the temperature range of 378-403 K and for a duration of 0.6-1.0 h. The rheological properties of tars modified with formaldehyde at 333, 343, and 353 K were studied and a comparison of the rheological properties of the obtained bituminous binder materials with oxidized bitumens was carried out.

**Keywords:** tar, bitumen, formaldehyde, chemical modification.

## 1. Introduction

In order to increase the service life of the asphalt pavement, and also, taking into account that the main binding component of the asphalt concrete mixture is bitumen, it is most appropriate to regulate the properties of the binder itself in order to meet all the needs that are required from the road surface. In particular, to ensure resistance to the influence of climatic conditions in the region where the covering will be laid and to the action of traffic loads. From this point of view, the rheological properties of bitumen play a significant role.[1]

Thus, from a functional point of view, bitumen must be sufficiently fluid at high temperature (≈ 433 K) to be pumped and used to create a uniform coating with mineral materials after mixing. In addition, it must be stiff enough at high temperatures to resist rutting (corresponding to local temperatures, ≈ 333 K). Finally, it must remain sufficiently ductile and elastic at low temperatures to resist cracking.

At the same time, the listed requirements are often difficult to fulfill for most unmodified bitumens, both distillation and oxidized. In addition, in some applications, the performance of unmodified bitumens may not be satisfactory, given the required performance properties, because they are brittle in cold environments and show poor heat resistance as the temperature increases. This limited operating temperature range is the main disadvantage of unmodified bitumen, which prevents its further use in road construction. In addition, as traffic speeds and loads continue to increase, unplanned overloading significantly shortens the life of asphalt pavements, increasing maintenance costs and risks to users. For this purpose, various additives and modifiers are used to improve the operational properties of bitumen, which can generally be divided into two types – physical and chemical.

Considering physical modifiers, it is worth noting that this type of modifiers does not chemically interact with the constituent components of bitumen, and the increase in key indicators (SP and E298), which are most often used to determine the effectiveness of the modification process, occurs only as a result of the physical process – mixing. In view of this, physical modification is also called mechanical. Physical modifiers are divided into groups according to the principle of action:

– thermoplastics (increase SP);
– elastoplasts (increase E298);
– thermoplastic elastomers (increase SP and E298).

A large number of conducted studies have shown both advantages and disadvantages of bitumen modification with polymers.[2] Benefits include that physical modification improves elasticity, resistance to cracking at low temperatures and resistance to rutting at high temperatures. Disadvantages include thermal instability and problems with the homogeneity of the obtained bitumen-polymer mixtures. Another method used to improve the properties of bituminous materials is chemical modification, which uses a chemical agent to change the properties of the original binder material due to its interaction with the bitumen components.

[1] Lviv Polytechnic National University, 12 S.Bandery St., Lviv 79013, Ukraine
[2] Danylo Halytsky Lviv National Medical University, 69 Pekarska St., Lviv 79010, Ukraine
✉ *yuriy_demchuk@ukr.net*

To date, many chemicals are used to modify bitumens, such as:

1) sulfur (S) Sakib *et al.*;[3]
2) polyphosphoric acid (PPA);[4]
3) sulfonic acids;[5]
4) siliconorganic compounds;[6]
5) thiourea dioxide;[7]
6) nanocomposites – polymer/clay, $TiO_2$, $Al_2O_3$, *etc.*;[8-10]
7) maleic anhydride (MA);[11]
8) thermoplastics, namely:
– reactive terpolymers – RET;[12]
– epoxy resins;[13,14]
– phenol-formaldehyde resins;[15,16]
– polyester resins.[17]

However, of the chemical modifiers listed above, only a few are practically used, namely: sulfur, PPA, MA, and thermoplastics, which are the most common chemical modifiers.

Separately, formaldehyde should be singled out among the chemical modifiers added to oil residues. In particular, given that the modification process produces new binding materials for road construction, which have higher viscosity compared to the raw material (tar) and meet the requirements for different brands of road viscous petroleum bitumen according to their characteristics. Among the advantages of this modification method, which distinguish it from other methods, the fact that the polymer (arene-formaldehyde resins), necessary for the process, is formed directly during modification from the components of the raw material (tar) and does not require further extraction from the mixture is also highlighted. This allows reducing the number of stages in the technological chain of obtaining modified bitumen to one, which is also a significant advantage of the introduction of this modifier.

The Department of Chemical Technology of Oil and Gas Processing of Lviv Polytechnic National University is actively conducting research related to the production of areno-[22-25] and phenol-formaldehyde[26,27] resins with the subsequent production of bituminous materials with improved operational properties.

The aim of this work was to investigate in more detail the properties of tars modified with formaldehyde, to prove the feasibility and prospects of using the obtained binding materials in road construction.

## 2. Experimental

### 2.1. Materials

From the preliminary results obtained by the authors,[23-25] it was established that the optimal raw material for obtaining new binding materials by chemical modification with formaldehyde is the residue from the vacuum distillation of oil – tar (samples T1 and T2). Tar samples were taken at JSC Ukrtatnafta (Ukraine). Characteristics of the initial materials are given in Table 1.

**Table 1.** Physico-chemical properties of tars (T1 and T2) and oxidized bitumens (OB2 and OB5)

| Index | Unit of measurement | Material | | | |
|---|---|---|---|---|---|
| | | T1 | T2 | OB2 | OB5 |
| Density at 293 K | $kg/m^3$ | 982.9 | – | – | – |
| Initial boiling point | K | 659 | – | – | – |
| Flashpoint | K | 555 | – | – | – |
| Penetration at 298 K | dmm | 247 | 208 | 82 | 75 |
| Softening point (SP) | K | 312.0 | 314.2 | 320.2 | 321.8 |
| Ductility at 298 K | cm | 58.1 | >100 | >150 | >150 |
| Fraass breaking point (FBP) | K | 255.0 | 244.0 | 261.0 | 249.0 |
| Plasticity interval (PI) | K | 57.0 | 70.2 | 59.2 | 72.8 |
| Penetration index | – | 0.62 | 0.69 | -0.71 | -0.51 |
| Resistance to hardening at 436 K (RTFOT method): | | | | | |
| mass change | wt. % | 0.35 | 0.37 | 0.13 | 0.09 |
| softening point after RTFOT | K | 318.6 | 321.2 | 326.0 | 330.0 |
| penetration at 298 K after RTFOT | dmm | 91 | 88 | 48 | 43 |
| softening point change | degree | 6.6 | 7.0 | 5.8 | 8.2 |
| retained penetration | % | 36.8 | 42.3 | 58.5 | 58.0 |
| Adhesion to gravel | mark | 2.5 | 2.5 | 3.0 | 2.5 |
| Adhesion to glass | % | 42 | 36 | 29 | 31 |

## 2.2. Preparation of Modified Binders

Chemical modification with formalin without stirring was carried out in hermetic stationary reactors capable of working under excess pressure (Fig. 1). This is due to the toxicity (according to **NFPA 704**) and the ability to evaporate formaldehyde at the operating temperature of the process (333-433 K). First, the formulating agent (a mixture of formalin and catalyst in a certain ratio) was prepared separately. First, tar (oil residue) or oxidized bitumen and solvent (if necessary) were loaded into the reactor and mixed until a homogeneous mass was reached. After cooling the mixture, the formulating agent was added. The reactor was hermetically closed and placed in a silicone bath heated to the required temperature, and the time of the start of the chemical modification process was fixed. At the end of the modification process, the depressurized container was placed in a vacuum cabinet to remove water and unreacted components. Vacuum drying was carried out for 4 h at 393 K and a pressure of less than 10 mm Hg.

**Fig. 1.** View of reactors for modification of tar or bitumen with formaldehyde without stirring

After vacuum drying of the obtained products, their analysis was carried out according to the indicators that are standardized for bituminous materials. In order to obtain modified bitumens for testing them in asphalt concrete, a reactor with a larger volume was used. Performance characteristics of the products obtained under the same conditions of modification of oil residues and bitumen with formaldehyde when using small and large volume reactors practically did not differ. This also indicates the effectiveness of using reactors without mixing.

## 2.3. Test Methods

The physico-chemical properties of tars (T1 and T2) and oxidized bitumens (OB2 and OB5) were studied according to the methods described in the literature.[20-25]

The adhesion of oil residues and bitumen to the surface of stone mineral material was determined using granite crushed stone (S1) from natural stone of the necessary fractions selected at LLC Novograd-Volyn Stone Crushing Plant. The adhesion of the binders to the surface of the stone material was studied according to the methods described in the elsewhere.[26,27]

## 3. Results and Discussion

The comparison of binding materials obtained by the traditional method – oxidation of oil residues with FMT was carried out according to the scheme shown in Fig. 2. Two samples of oxidized bitumen, OB2 and OB5, respectively, were obtained from two tar samples (T1 and T2) at the industrial plant. The main factors controlling the oxidation process are presented in Table 2. Tars modified with formaldehyde (from T1 FMT-1, FMT-2 and FMT-3 were obtained; T2 – FMT-8 and FMT-9) were obtained using concentrated sulfuric acid as a process catalyst according to optimal values of process control factors were found (Table 3). It was also established[23-25] that other inorganic acids (HCl and $H_3PO_4$) are effective catalysts of the process. Therefore, for comparison, FMT was obtained using concentrated hydrochloric and orthophosphoric acids as catalysts of the process with the values of the factors that coincide with the use of sulfuric acid (Table 3). The formalin/catalyst mass ratio for all FMTs is the same and equal to 1.0. The temperature and duration of modification also do not differ significantly and are 373-403 K and 0.6-1.0 h, respectively. The only difference is the amount of the modifier – formulating agent (a mixture of formalin and catalyst in a certain ratio). To obtain a bituminous material with approximately the same SP, a different amount of formulating agent is required depending on the nature of the catalyst used. For example, FMT-8, FMT-10 and FMT-11 were obtained from T2, which are characterized by approximately the same SP: 325.4; 321.8 and 324.2 K, respectively. They differ in the amount and composition of the formulating agent: FMT-8 – 4.0 wt. % per raw material (2.0 wt. % of formalin and 2.0 wt. % of concentrated sulfuric acid); FMT-10 – 6.0 wt. % for raw materials (3.0 wt. % of formalin and 3.0 wt. % of concentrated hydrochloric acid); FMT-11 – 6.0 wt. % for raw materials (3.0 wt. % of formalin and 3.0 wt. % of concentrated orthophosphoric acid).

The selected tars (T1 and T2) are characterized by high values of P298 – 247 and 208 dmm (Fig. 3) and low values of SP – 312.0 and 314.2 K (Fig. 4), which does not allow them to be used as binding materials in road construction.

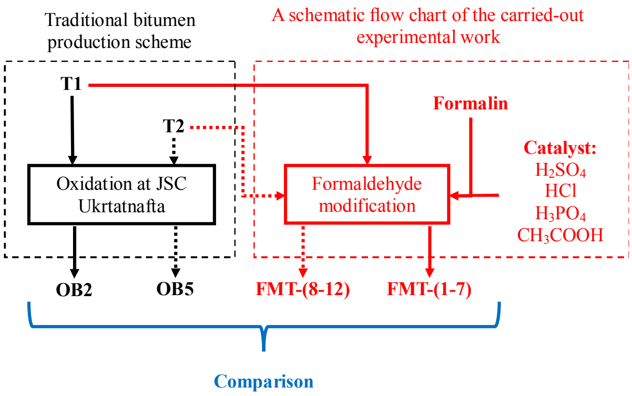


**Fig. 2.** Scheme of comparison of the obtained traditional and researched binders

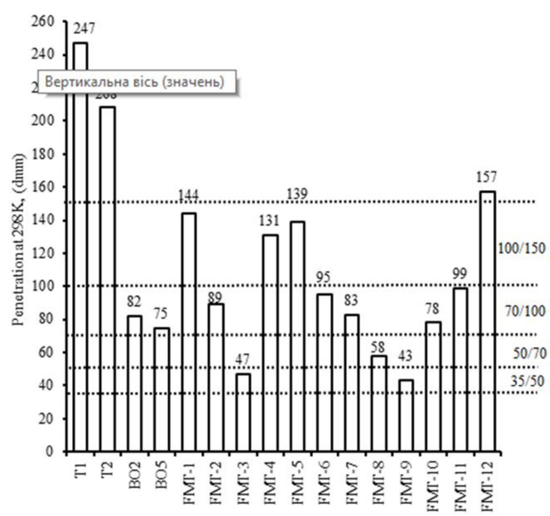


**Fig. 3.** Bitumen comparison for P298

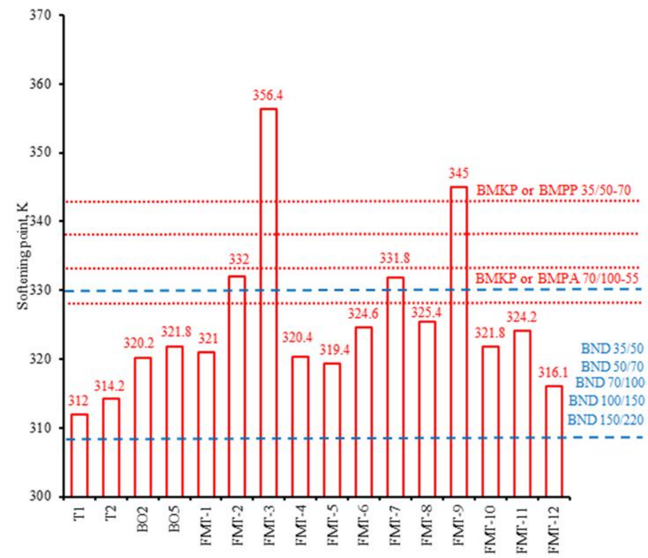


**Fig. 4.** Comparison of bitumens by SP

Guided by the current Ukrainian regulatory documents, the obtained FMT samples correspond to the brands of binding materials in terms of their main physical and mechanical properties (Table 4, Figs. 3 and 4):

bitumen petroleum road viscous according to **DSTU 4044:2019**:[28]

- BND 150/220 – FMT-12;
- BND 100/150 – FMT-1, FMT-4, FMT-5;
- BND 70/100 – FMT-2, FMT-6, FMT-7, FMT-10, FMT-11;
- BND 50/70 – FMT-8;

**Table 2.** Control parameters of the tar oxidation process with air at JSC Ukrtatnafta (Kremenchuk, Ukraine)

| Variable parameter of process | Units | Value | |
|---|---|---|---|
| Raw materials | – | T1 | T2 |
| Product (oxidized bitumen) | – | OB2 | OB5 |
| Consumption of raw materials | $m^3$/hour | 45.0 | 13.0 |
| | tons/hour | 45.0 | 13.0 |
| Air consumption | $m^3$/hour | 4300 | 1300 |
| | tons/hour | 5.547 | 1.677 |
| Specific consumption | $\frac{m^3 \text{ of air}}{m^3 \text{ of raw materials}}$ | 95.6 | 100 |
| | $\frac{\text{tons of air}}{\text{tons of raw materials}}$ | 0.123 | 0.129 |
| Nitrogen consumption | $m^3$/hour | 260 | 75 |
| Oxidation duration | hour | 2,5 | 8,6 |
| Temperature of feed of raw materials to the oxidation column | K | 451 | 444 |
| Excess pressure in the oxidation column | kg/$cm^3$ | 0 | 0 |
| Temperature of the bottom of the oxidation column | K | 453 | 444 |
| Temperature of the top of the oxidation column | K | 388-392 | 372-377 |

**Table 3.** Control parameters of the process of chemical modification of tars (T1 and T2) with formaldehyde

| Variable parameter of process | Units | FMT-1 | FMT-2 | FMT-3 | FMT-4 | FMT-5 | FMT-6 | FMT-7 | FMT-8 | FMT-9 | FMT-10 | FMT-11 | FMT-12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Raw materials | – | T1 | | | | | | | T2 | | | | |
| Amount of solvent | wt. % per raw material | without solvent | | | | | | | | | | | |
| Amount of formalin (including formaldehyde) | wt. % per raw material | 1.0 | 1.9 | 3.0 | 3.2 | 1.0 | 2.0 | 3.0 | 1.0 | 2.0 | 3.0 | 3.0 | 3.0 |
| Type of process catalyst | – | $H_2SO_4$ | | | HCl | $H_3PO_4$ | | | $H_2SO_4$ | | HCl | $H_3PO_4$ | $CH_3COOH$ |
| Amount of catalyst | wt. % per raw material | 1.1 | 1.7 | 3.2 | 3.1 | 1.0 | 2.0 | 3.0 | 1.0 | 2.0 | 3.0 | 3.0 | 3.0 |
| Mass ratio formalin / catalyst | – | 0.91 | 1.12 | 0.94 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | | 1.0 | 1.0 | 1.0 |
| Modification temperature | K | 383 | 378 | 383 | 373 | 403 | 403 | 403 | 403 | | 403 | 403 | 403 |
| Duration of modification | hours | 0.6 | 0.6 | 0.8 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | | 1.0 | 1.0 | 1.0 |

**Table 4.** Physico-mechanical properties of tars (T1 and T2), oxidized bitumens (OB2 and OB5) and tars modified with formaldehyde (FMT)

| Nr. | Index | T1 | T2 | OB2 | OB5 | **FMT-1** | **FMT-2** | **FMT-3** | **FMT-4** | **FMT-5** | **FMT-6** | **FMT-7** | **FMT-8** | **FMT-9** | **FMT-10** | **FMT-11** | **FMT-12** | BND 100/150 (according to **DSTU 4044:2019**[28]) | BND 70/100 (according to **DSTU 4044:2019**[28]) | BMPA 70/100-55 (according to **DSTU 9116:2021**[29]) | BMPP 35/50-70 (according to **DSTU 9116:2021**[29]) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 61 | Penetration at 298 K (P298), dmm | 247 | 208 | 82 | 75 | 144 | 89 | 47 | 131 | 139 | 95 | 83 | 58 | 43 | 78 | 99 | 157 | 101-150 | 71-100 | 71-100 | 35-50 |
| 2 | Softening point (SP), K | 312.0 | 314.2 | 320.2 | 321.8 | 321.0 | 332.0 | 356.4 | 320.4 | 319.4 | 324.6 | 331.8 | 325.4 | 345.0 | 321.8 | 324.2 | 316.1 | 314-320 | 318-324 | ≥ 328 | ≥ 335 |
| 3 | Ductility at 298 K (D298), cm | 58.1 | >100 | >150 | >150 | 42 | 16 | 4 | 59 | 79 | 111 | 134 | 15 | 12 | >100 | 86 | >100 | ≥ 70 | ≥ 60 | – | – |
| 4 | Fraass breaking point (FBP), K | 255 | 244 | 261 | 249 | 256 | 258 | 264 | 259 | 253 | 256 | 259 | 253 | 256 | 249 | 250 | 247 | ≤ 257 | ≤ 260 | ≤ 255 | ≤ 260 |
| 5 | Penetration index | 0.62 | 0.69 | -0.71 | -0.51 | 1.45 | 2.49 | 4.61 | 0.89 | 0.80 | 0.95 | 2.22 | -0.26 | 2.76 | -0.40 | 0.98 | 0.15 | –2 till +1 | | – | – |
| 6 | Plasticity interval (PI), K | 57.0 | 70.2 | 59.2 | 72.8 | 65.0 | 74.0 | 92.4 | 61.4 | 66.4 | 68.6 | 72.8 | 72.4 | 89.0 | 72.8 | 74.2 | 69.1 | – | – | – | – |
| 7 | Adhesion to glass, % | 42 | 36 | 29 | 31 | 65 | 81 | 94 | 83 | 89 | 97 | 94 | 78 | 96 | 92 | 83 | 80 | >16 | >18 | >75 | >75 |
| 8 | Adhesion to gravel (S1), mark | 2.5 | 2.5 | 3.0 | 2.5 | 3.5 | 4.5 | 5.0 | 4.5 | 4.5 | 5.0 | 5.0 | 4.5 | 5.0 | 5.0 | 4.5 | 4.5 | – | – | >4.5 | >4.5 |
| 9 | Resistance to hardening at 436 K (RTFOT method) | | | | | | | | | | | | | | | | | | | | |
| 9.1 | softening point change, degree | 6.6 | 7.0 | 5.8 | 8.2 | 6.0 | 5.2 | 4.5 | 5.8 | 4.6 | 5.2 | 5.4 | 6.0 | 4.2 | 7.4 | 7.6 | 7.9 | – | – | <6 | <5 |
| 9.2 | retained penetration, % | 36.8 | 42.3 | 58.5 | 58.0 | 62.3 | 79.5 | 88.7 | 66.6 | 66.9 | 78.4 | 88.0 | 76.7 | 86.5 | 62.6 | 80.8 | 58.2 | – | – | >75 | >75 |
| 9.3 | mass change, wt.% | 0.35 | 0.37 | 0.13 | 0.09 | 0.40 | 0.35 | 0.25 | 0.18 | 0.27 | 0.39 | 0.46 | 0.37 | 0.27 | 0.28 | 0.32 | 0.48 | – | – | – | – |

bitumen modified with polymers (according to SP) according to **DSTU 9116:2021:**[29]

- BMPA 70/100-55 − FMT-2, FMT-7;
- BMPA 35/50-70 − FMT-3, FMT-9;

bitumen modified with synthetic waxes according to **SOU 42.1-37641918-068:2017:**[30]

- BMW-S 60/90 – FMT-2, FMT-7;
- BMW-S 40/60 – FMT-3, FMT-9;

bitumen modified with adhesive additives according to **SOU 45.2-00018112-067:2011:**[31]

- BND-A 70/100 – FMT-6, FMT-7, FMT-10;
- BND-A 35/50 – FMT-3, FMT-9.

That is, this method allows obtaining almost any bituminous materials for road construction.

Intensification of the modification process (reduction of P298 and increase of SP) depends on the amount of formulating agent. To obtain bitumens with high SP (FMT-3 and FMT-9) a larger amount of modifier (formulating agent) is required. These data indicate the high flexibility of this process, in contrast to the traditional oxidation process, in which it is not possible to obtain such bitumens. Also, the advantage of the process of chemical modification of tar with formaldehyde (Table 3; up to 1.0 h) in comparison with oxidation (Table 2; 2.5-8.6 h) is a significantly shorter reaction time.

The data presented in Table 4 and Figs. 3 and 4 confirm that inorganic acids are the most effective catalysts for the process of chemical modification of tars with formaldehyde. If inorganic acids are compared with each other, their efficiency can be placed in the following order: $H_2SO_4 \rightarrow H_3PO_4 \rightarrow HCl$. If we talk about their shortcomings, then concentrated sulfuric acid is capable of sulfonation reaction of aromatic structures of bitumen, and the use of concentrated hydrochloric acid intensifies the corrosion processes of equipment, which requires the use of special expensive alloys during the construction of the installation. Concentrated orthophosphoric acid is devoid of these disadvantages. It should also be noted about another advantage of using orthophosphoric acid, which allows obtaining bituminous materials with higher values of the D298 indicator, which indicates the plasticizing effect of this acid.

A significant advantage of the process of chemical modification of tar with formaldehyde is that the obtained materials with approximately the same SP (Fig. 4) – 320.2-324.2 K have a higher value of the P298 index in comparison with the oxidation process. This can be explained by the fact that the oxidation process of tar with air oxygen at 444-453 K (Table 2) leads to the thermo-oxidative destruction of paraffin and naphthenic hydrocarbon structures (oxidation gases and black solar are formed in the process), which leads to an increase in hardness and a decrease in plasticity of the obtained products. In the process of chemical modification of tar with formaldehyde, which takes place at lower temperatures (Table 3) and without the participation of oxygen, the probability of such processes is much lower, these paraffin and naphthenic structures remain in the product, which leads to high values of P298. Such bituminous materials (FMT) are good raw materials for the modification process with polymers (for example, SBS, terpolymers, waxes, *etc.*) in which P298 is significantly reduced. It will also allow reducing the polymer content, which will be necessary to bring the E298 indicator to the required values.

Rheological studies at temperatures of 333, 343, and 353 K were performed on a Brookfield rotary viscometer according to DSTU EN 13302:2019.[32] T2, FMT-8, FMT-10, and FMT-11 with P298 and SP − 208 and 314.2 were used for the tests; 58 and 325.4; 78 and 321.8; 99 and 324.2 K, respectively. FMTs were obtained using different catalysts (Table 3), namely FMT-8 – $H_2SO_4$, FMT -10 – HCl, FMT -11 – $H_3PO_4$. The test results are shown in Figs. 5-7.

According to DSTU EN 12591:2017,[33] for bitumen 100/150, the dynamic viscosity at 333 K should be greater for bitumen 70/100 − ≥90, 50/70 − ≥145, 35/50 − ≥225 Pa·s. Dynamic viscosity at 333 K is a fundamental property of the binder, which characterizes the heat resistance of the coating (resistance to rutting). SP is an analogue of this indicator, which is an empirical indicator that does not always reflect the behavior of the binder at high operating temperatures. FMT-10 and FMT-11 according to the P298 indicator belong to bitumen grade 70/100, and FMT-8 to 50/70 (Table 4, Fig. 3). In the process of oxidation at JSC Ukrtatnafta tar (T2), the dynamic viscosity at 333 K increases from 38.8 to 204.8 Pa·s and bitumen 70/100 is obtained. The process of chemical modification of tar with formaldehyde allows to significantly increase the dynamic viscosity at 353 K of the obtained products (especially when used as a catalyst for the orthophosphoric acid process).

It should also be emphasized that when concentrated hydrochloric acid is used as a catalyst in the process of tar modification with formaldehyde, it is removed from the bituminous material during vacuum drying, as it has a low boiling point (321 K). Unlike sulfuric and orthophosphoric acids, which have high boiling points and, accordingly, remain after vacuum drying in FMT (especially sulfuric). In our opinion, this significantly affects the rheological properties of the obtained bituminous materials, which is confirmed by experimental studies.

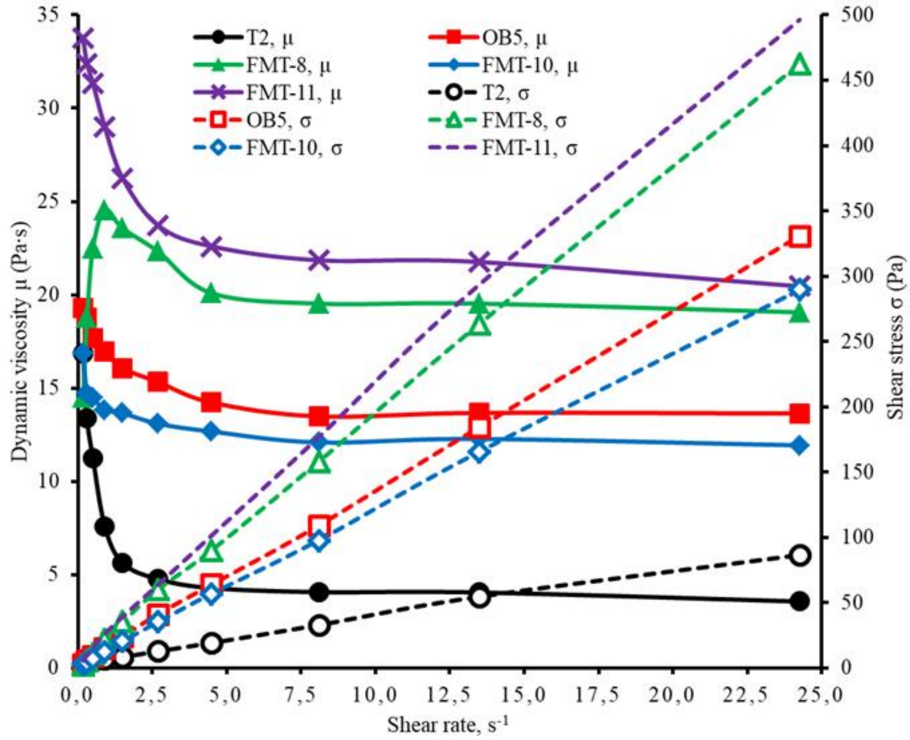


**Fig. 5.** Dependence of dynamic viscosity (μ) and shear stress (σ) of studied bitumens on shear rate at a temperature of **333 K**

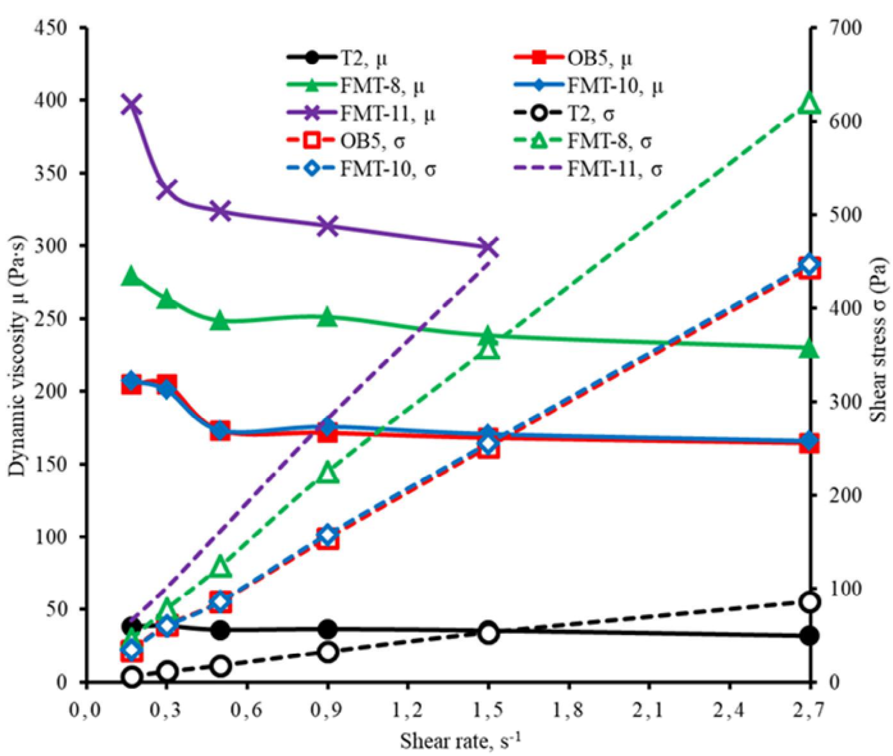


**Fig. 6.** Dependence of dynamic viscosity (μ) and shear stress (σ) of studied bitumens on shear rate at a temperature of **353 K**

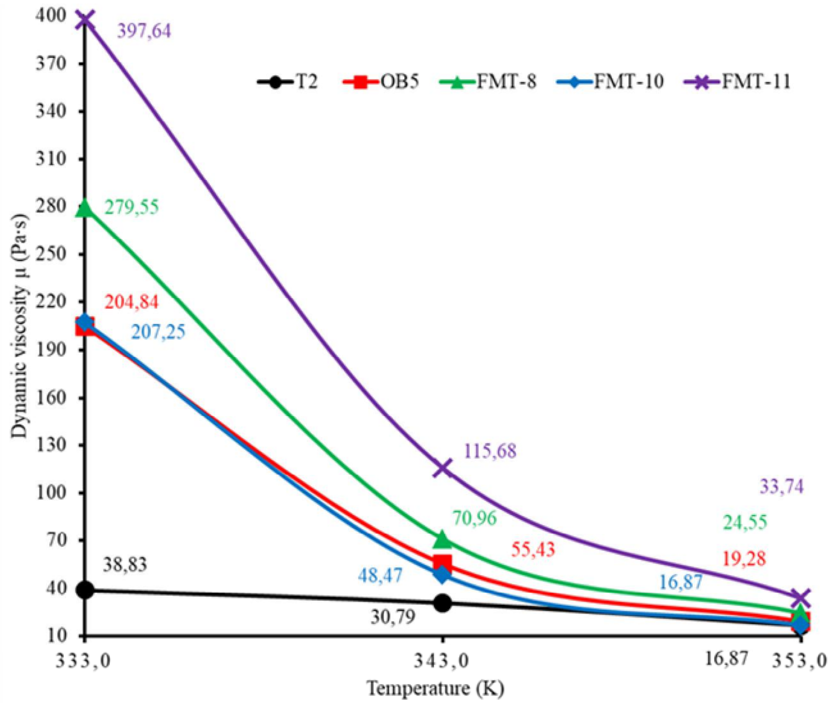


**Fig. 7.** The effect of temperature (in the range of 333-353 K) on the dynamic viscosity (μ) of the tested bitumens

FMT-10, which is obtained by using HCl in terms of rheological properties, is almost identical to oxidized bitumen (OB5), since the curves in Figs. 5-7 practically overlap. P298 and SP are also not significantly different for OB5 and FMT-10 (Table 4).

FMT-11 obtained using $H_3PO_4$ is characterized by the highest viscosity values (Figs. 5-7), while possessing the highest values of P298 and SP, 99 dmm and 324.2 K, respectively, among all bituminous materials studied. That is, orthophosphoric acid performs a plasticizing function, which is an important factor at low operating temperatures of such materials and leads to a decrease in the intensity of cracking of such a coating.

Greater hardness and lower plasticity of FMT-8 is confirmed by rheology studies (Figs. 5-7). Having the lowest values of P298 (58 dmm) and the highest value of SP (325.4 K), the position of the viscosity-temperature curve is not the highest (Fig. 7). This also confirms a greater tendency to form gel-like structures. When using this type of binder, the additional use of plasticizing additives is also desirable.

## 4. Conclusions

A new approach to obtaining bituminous materials for road construction by the method of chemical modification of tars with formalin (formaldehyde) is proposed. It has been confirmed that, depending on the amount of modifier (up to 3.0 wt. %), it is possible to obtain binders from tar that correspond in physical and mechanical properties to traditional viscous road petroleum bitumens, bitumens modified with polymers (with the exception of the elasticity indicator at 298 K ), bitumen modified with synthetic waxes and bitumen modified with adhesive additives. That is, this technology makes it possible to obtain almost any type of binding material for road construction from tar, which is a significant advantage compared to the traditional scheme of bitumen production, which requires at least two stages – oxidation or deep vacuum distillation and the addition of polymer modifiers. It was established that depending on the type of catalyst used, the rheological behavior of the obtained binding materials is different. The tars modified with formaldehyde obtained with the use of concentrated orthophosphoric acid as a process catalyst have the highest dynamic viscosity.

## Acknowledgements

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## Abbreviations

D298 Ductility at 298 K (cm)
E298 Elastic recovery at 298 K ( %)
FBP Fraas breaking point (K)

FMT Formaldehyde modified tar
OB Oxidized bitumen
P298 Penetration at 298 K (dmm)
PI Plasticity interval (K)RTFOT Rolling thin film oven test
SP Softening point (K)
T Tar

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## ОДЕРЖАННЯ БІТУМУ, МОДИФІКОВАНОГО НИЗЬКОМОЛЕКУЛЯРНИМИ ОРГАНІЧНИМИ СПОЛУКАМИ ІЗ НАФТОВИХ ЗАЛИШКІВ. 8. ПЕРСПЕКТИВИ ВИКОРИСТАННЯ ГУДРОНІВ, МОДИФІКОВАНИХ ФОРМАЛЬДЕГІДОМ, У ДОРОЖНЬОМУ БУДІВНИЦТВІ

***Анотація.*** *Проведено модифікування гудронів формаліном (37 %-м водним розчином формальдегіду) із використанням різних кислот, як каталізаторів процесу, із метою одержання нових в'яжучих матеріалів для дорожнього будівництва. Як каталізатор використовували* $H_2SO_4$, *HCl,* $H_3PO_4$ *та* $CH_3COOH$. *Процес модифікування проводили в діапазоні температур 378-403 К та тривалості 0,6-1,0 год. Досліджено реологічні властивості гудронів, модифікованих формальдегідом, за 333, 343 та 353 К, та проведено порівняння реологічних властивостей отриманих бітумних в'яжучих матеріалів з окисненими бітумами.*

***Ключові слова:*** *гудрон, бітум, формальдегід, хімічне модифікування.*