PETROLEUM AND GAS PROCESSING

HIGH-PRESSURE HYDROTREATING OF PETROLATUM FROM MIXED ZHIRNOVSK AND KOROBKI CRUDES

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Catalytic hydrogenation processes are used widely, not only in the production of fuels and oils, but also in the production of highly treated paraffin waxes, ceresins,* and petrolatums [1-4].

The characteristic feature in the hydrotreating of high-molecular-weight solid hydrocarbons is the use of moderate temperature to avoid decomposition of the feedstock. The high-molecular-weight nitrogen, sulfur, and oxygen compounds in residual stocks are considerably more difficult to hydrogenate than the analogous compounds of lower molecular weight. Hence, in order to achieve the required treating level for petrolatums, ceresins, and microcrystalline waxes, the process must be conducted at a high hydrogen pressure (up to 300 kg/cm^2). The conditions of the hydrogenation process and the nature and extent of the reactions that occur will depend largely on which catalyst is used, and on the catalyst condition.

From the patent literature, certain catalysts are known to be used in hydrotreating ceresins, petrolatums, and paraffin waxes. These include alumina–cobalt–molybdenum [5, 6], alumina–nickel–molybdenum [7-9], alumina–chromium–molybdenum [9], nickel on aluminum oxide or silica gel [10-12], cobalt or molybdenum on aluminum oxide [5], nickel–tungsten–iron in sulfided form [13], and others.

In the work reported here, we used a standard alumina–cobalt–molybdenum catalyst, and in certain experiments an alumina–nickel–molybdenum catalyst.

The alumina–cobalt–molybdenum catalyst contained 12.6% by wt. of molybdenum oxide, 4.2% cobalt oxide, remainder aluminum oxide and impurities. The alumina–nickel–molybdenum catalyst consisted of 14.0% molybdenum oxide, 8.4% nickel oxide, remainder aluminum oxide and impurities.

This study was aimed at selecting process conditions to obtain a white petrolatum (not less than 260 mm with a No. 1 glass in a KN-51 instrument at a dilution of 1:20) without any breakdown of the paraffinic-naphthenic hydrocarbons. The hydrogenation was carried out in a flow-type pilot unit with a reaction volume of 200 cm^3, with descending flow of the gas–feedstock mixture. The hydrogen content of the hydrogen-rich gas was held at a level of 90% by volume; the catalyst was charged in a crushed form (grain size 2-3 mm). The experiments were begun by sulfiding the catalyst, by passing through the reactor a mixture of hydrogen-rich gas with a straight-run fraction distilling at 200-360°C and containing 1.2% sulfur by weight. Then, over a 24-h period, the catalyst was stabilized by operation on feedstock at a temperature of 350°C with a feedstock space velocity of 0.5 h^{-1}. The feedstock was a petrolatum obtained in the processing of mixed Volgograd crudes, this petrolatum representing a promising raw material for the production of high-melting ceresins and microcrystalline waxes [14]. The properties of the original petrolatum were as follows:

*The term "ceresin" in Russian practice denotes any high-melting mineral wax, whether derived from ozocerite or petroleum – Translator.

NV Bränch, Groznyi Petroleum Scientific-Research Institute. Angarsk Petrochemical Combine. Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 12, pp. 1-5, December, 1973.

Melting Point, °C	67
Dropping point, °C	72
Density at 90°C, g/cm^3	0.8080
Kinematic viscosity at 100°C, cSt	13
Average molecular weight	650
Oil content, wt. %	10.8
Penetration at 10°C with 100-g load	27.2

This program included a study of the effects of temperature, space velocity, and ratio of hydrogen-rich gas to feedstock on the quality of the hydrogenated products, the pressure being held constant at 300 kg/cm^2 in all experiments. Each series of experiments for investigating the effect of some one of the process parameters was carried out with a single batch of catalyst. The treating level was determined according to the degree of hydrogenation of the sulfur and nitrogen compounds and aromatic hydrocarbons present in the original petrolatum, and also according to the change in color of the petrolatum. The degree of petrolatum decomposition was judged by the increase in content of light fractions distilling below 460°C, and by the change in potential content of Grade 75 [75°C melting point] ceresin.

The effect of temperature on the hydrogenation of petrolatum was studied at temperatures of 300-440°C on alumina–cobalt–molybdenum catalyst, and at 330-400°C on alumina–nickel–molybdenum catalyst, with a feedstock space velocity of 0.5 h^{-1} and a volume ratio of hydrogen-rich gas to feedstock of 1000:1 or 750:1; respectively. The results of this study, which are listed in Table 1, show that with either type of catalyst, at a temperature of only 330-335°C, a very thorough upgrading of the original petrolatum is observed. The content of nitrogen bases is reduced considerably, the degree of desulfurization reaches 75-79%, the content of aromatic hydrocarbons desorbed by benzene decreases from 2.5% to 1.0-0.3% by weight, and the content of resins from 1.1% to 0.5-0.3%. The polycyclic aromatic hydrocarbons are hydrogenated to a greater degree than the monocyclic, as indicated by the greater decrease in optical density of the petrolatum in the 324-330 mμ wavelength region, in comparison with the decrease in optical density in the 260-272 mμ region. The shift in the maximum in this latter region from 260 to 265-272 mμ indicates that the dehydrogenation of bicyclic and polycyclic aromatic hydrocarbons is proceeding with the formation of mixed paraffinic-naphthenic-aromatic structures. The color of the brown petrolatum becomes light yellow when hydrogenated on alumina–cobalt–molybdenum catalyst, and white (with a yellowish tinge) on alumina–nickel–molybdenum catalyst.

When the hydrogenation temperature is increased to 360°C, the degree of desulfurization reaches 80-83%, and the content of nitrogen bases is reduced to 10.0-9.0 mg NH_3/liter. The optical density of the petrolatum in the region of 260-272 mμ decreases by 90-97%, and in the 324-330 mμ region by 96-98%. At this process temperature, the hydrotreated petrolatum consists essentially of 100% paraffinic-naphthenic hydrocarbons, and it is white in color.

It can be seen from Fig. 1 that the physicochemical properties of the petrolatum do not change significantly when it is hydrotreated on alumina–cobalt–molybdenum catalyst at temperatures up to 360°C. Raising the temperature to 400°C brings about a slight decomposition of the petrolatum, as indicated by a decrease in viscosity from 12.3 to 11.0 cSt, an increase in penetration from 30 to 43.8, and an increase in the amount of light fractions distilling below 460°C from 4-5 to 13% by volume (see Table 1). However, the potential content of ceresins and microcrystalline waxes in the hydrotreated petrolatum remain unchanged. There is a sharp increase in petrolatum breakdown when the hydrogenation temperature is increased above 400°C. With hydrogenation temperatures of 430-440°C, the average molecular weight of the petrolatum is reduced from 650 to 318, the oil content increases to 32% by weight, and the content of fractions boiling below 460°C increases to 63% by volume; the other properties of the petrolatum are also changed. The potential content of ceresins and waxes in the petrolatum hydrotreated at these temperatures is reduced significantly.

It can be seen from Fig. 2 that, when the alumina–nickel–molybdenum catalyst is used in the hydrogenation, some decomposition of the petrolatum is observed even at 360-370°C, as indicated by a decrease in viscosity down to 11.4 cSt and an increase in penetration up to 41.0. The physicochemical properties of the petrolatum hydrotreated on alumina–nickel–molybdenum catalyst at 360°C are very close to those of the material hydrotreated on alumina–cobalt–molybdenum catalyst at 400°C. With the nickel catalyst, an increase in hydrogenation temperature from 360 to 400°C leads to a considerable increase in the degree of petrolatum breakdown, so that the product is similar in properties to that obtained on the cobalt catalyst at 430-440°C. The quantity of fractions boiling below 460°C increases up to 28% by volume, the melting point and dropping point decrease to 61 and 57°C, respectively, the average molecular weight decreases to 430, and the oil content increases to 28.6% by weight. The potential content of Grade 75 ceresin is reduced by a factor of 1.7.

TABLE 1. Results of Petrolatum Hydrotreating

	Original petrolatum	Petrolatum treated with alumina – cobalt – molybdenum catalyst					Petrolatum treated with alumina – nickel – molybdenum catalyst		
		300 °C	335 °C	360 °C	400 °C	440 °C	330 °C	360 °C	400 °C
Color									
Determined visually	Brown	Yellow	Light yellow	White	White	White	White with light yellow tint	White	White
In KN-51 instrument with No. 1 glass at 1/20 dilution, mm	20*	60	100	260	270	280	230	280	280
Sulfur content, wt. %	0,151	0,071	0,039	0,034	0,021	0,009	0,032	0,025	0,021
Content of nitrogen bases, mg NH_3/liter	90	57,4	21,8	10,0	8,5	5,6	13,7	9,4	7,9
Optical density in wavelength interval									
260–272 mμ (c=1g/l, L=10mm)	0,876	0,476	0,254	0,087	0,042	0,015	0,034	0,025	0,007
324–330 mμ (c=6g/l, L=10mm)	0,876	0,331	0,138	0,029	0,025	0,010	0,022	0,015	0,005
Separation with urea									
Hydrocarbons forming complex, wt. %	21,0	21,9	21,7	21,8	23,5	34,9	20,5	21,0	20,3
Melting point, °C	80,3	78,4	79,2	78,6	78,0	61,8	78,8	78,8	71,2
Hydrocarbons not forming complex, wt. %	79,00	78,1	78,3	78,2	76,5	65,1	79,5	79,0	79,7
Melting point, °C	48,8	48,8	48,2	48,2	46,6	32,0	47,2	47,4	36,0
Separation on silica gel									
Paraffinic-naphthenic hydrocarbons, wt. %	86,0	91,1	98,5	99,5	99,7	99,9	98,4	99,4	99,8
Melting point, °C	68,8	68,0	66,4	66,3	66,6	54,0	67,2	66,9	57,0
Refractive index n_D^{20}	1,4450	1,4429	1,4460	1,4436	1,4425	1,4260	1,4435	1,4424	1,4350
Aromatic hydrocarbons desorbed by isooctane, wt. %	10,4	6,8		None			1,0	0,3	None
Melting point, °C	52,6	49,4	—	—	—	—	51,4	—	—
Refractive index n_D^{20}	1,4701	1,4732	—	—	—	—	1,4735	—	—
Aromatic hydrocarbons desorbed by benzene, wt. %	2,5	1,4	1,0	0,3	0,2	0,1	0,3	0,2	0,1
Resins, wt. %	1,1	0,7	0,5	0,2	0,1	None	0,3	0,1	0,1
Fractions distilling below 460°C, vol. %	0	3	2	4	13	63	6	6	27
Potential content of Grade 75 ceresin, wt. %	62,7	66,8	66,9	65,4	65,8	32,7	62,7	63,4	35,4

*Determined with No. 2 glass.

Of interest is the increase in content of hydrocarbons forming complexes with urea in the petrolatum hydrotreated on the cobalt catalyst. With hydrogenation temperatures from 300 to 370°C, the content of these hydrocarbons is 22% by weight, at 400°C it is 23.5%, and at 440°C it has reached 34.9%. No such phenomenon was observed with the nickel catalyst, where the content of hydrocarbons forming complexes with urea remained at a level of 20-21% over the temperature range from 330 to 400°C, in spite of the fact that the degree of petrolatum breakdown had increased considerably at 400°C. This difference is apparently related to the difference in isomerization activity of the catalysts.

In a study of the effect of hydrogen/feedstock ratio and feedstock space velocity, at a hydrogenation temperature of 360°C, it was shown that increasing the feed of hydrogen-rich gas from 500 : 1 up to 1500 : 1 (volumes/volume feedstock) gives only a very slight improvement in the color of the product. Also, the physicochemical properties of the hydrotreated petrolatum and the potential contents of solid hydrocarbons having various melting points were essentially unchanged.

In the hydrotreating with a feedstock space velocity of 0.5 h^{-1}, a hydrogenated product with a pure white color could be obtained. When the feedstock space velocity was increased up to 0.8 h^{-1} or higher, the degree of hydrogenation was lower and the petrolatum color poorer. The degree of desulfurization also dropped off.

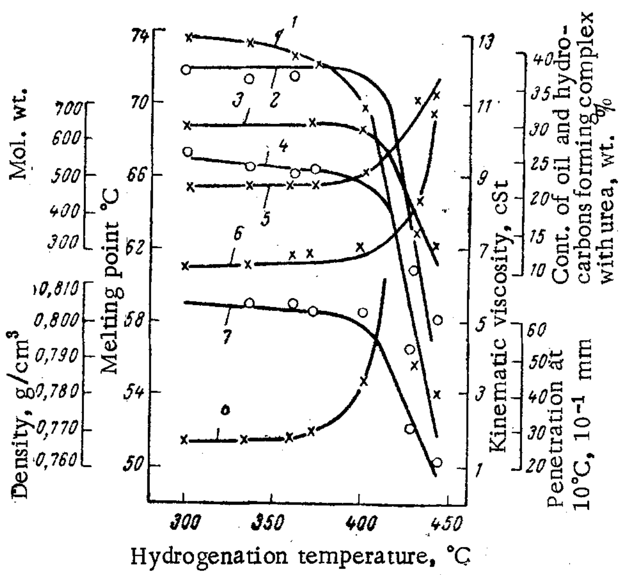

Fig. 1

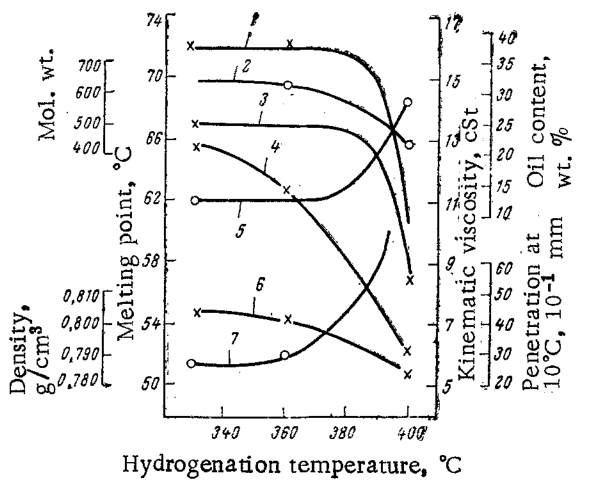

Fig. 2

Fig. 1. Physicochemical properties of petrolatum vs. temperature of hydrogenation with alumina–cobalt–molybdenum catalyst: 1) kinematic viscosity at 100°C; 2) dropping point; 3) average molecular weight; 4) melting point; 5) content of hydrocarbons forming complex with urea (wt. %); 6) oil content (wt. %); 7) density at 90°C; 8) penetration at 10°C.

Fig. 2. Physicochemical properties of petrolatum vs. temperature of hydrogenation with alumina–nickel–molybdenum catalyst: 1) dropping point; 2) average molecular weight; 3) melting point; 4) kinematic viscosity at 100°C; 5) oil content (wt. %); 6) density at 90°C; 7) penetration at 10°C.

The results of this investigation have shown that, in order to obtain petrolatum of a pure white color without breakdown of the paraffinic-naphthenic hydrocarbons, the hydrogenative treating must be carried out under the following process conditions:

Feedstock space velocity, h^{-1}	0.5
Hydrogen-rich gas, volumes per volume feedstock	750:1
Temperature, °C	360-400
Catalyst	Alumina–cobalt–molybdenum
Temperature, °C	340-370
Catalyst	Alumina–nickel–molybdenum

A stability test on the alumina–cobalt–molybdenum catalyst showed that, under the recommended processing conditions, its catalytic activity is maintained at a high level for at least one thousand hours. The petrolatum and the ceresins and waxes recovered from the petrolatum have a white color and meet the purity requirements imposed by the paper, packaging, electrotechnical, perfume, and pharmaceutical industries, which are consuming ever-increasing quantities of such products.

SUMMARY

1. By hydrotreating a petrolatum from mixed Zhirnovsk and Korobki crudes at a pressure of 300 kg/cm², feedstock space velocity of 0.5 h^{-1}, hydrogen-rich gas 750 volumes per volume of feedstock, and temperatures of 360-400°C on alumina–cobalt–molybdenum catalyst or 340-370°C on alumina–nickel–molybdenum catalyst, white petrolatum can be obtained without any breakdown of the paraffinic-naphthenic hydrocarbons.

2. From a comparison of the results obtained in hydrogenating petrolatum on both types of catalysts, it has been shown that the alumina–nickel–molybdenum catalyst manifests a somewhat greater hydrogenating activity, but at the same time gives more cracking and isomerization.

3. The hydrotreated petrolatum is a high-quality raw material for the production of highly treated ceresins and waxes.

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