

## *Studies on Micro-paraffin. VI. Properties of the Micro-paraffin*

By Kazuo NEGORO

(Received March 22, 1961)

Although micro-paraffin has been reported<sup>1)</sup> to consist of side-chain hydrocarbons, the author has considered the problem from different standpoints and has confirmed that micro-paraffin contains a considerable amount of straight-chain compounds and that the carbon number is slightly larger than that of crystalline paraffins<sup>2,3)</sup>. When crystalline wax or *n*-dotriacontane was crystallized in the presence of those organic compounds with a hydroxyl group attached to the benzene ring and of a similar molecular structure, it was observed that micro-crystallization occurred<sup>4)</sup>. The alcohol-extracted fraction obtained by chromatography from those asphalt components which had been isolated from micro-paraffin was also found to give micro-crystallization effects, and its ultraviolet and infrared spectra revealed that it also had the same hydroxyl groups and benzene ring as other pure organic compounds.

The present paper deals with the properties of the micro-paraffin from the above viewpoints.

### Results and Discussion

#### **The Micro-crystallizing Properties of the Micro-paraffin are Caused by Secondary Factors.**

—Although micro-paraffin has previously been reported to consist mainly of isoparaffin<sup>5,6)</sup>, about 60% of the micro-paraffins have been found by the present study to be urea-adductible when treated by the urea method. None of these urea-adductible paraffins are *n*-paraffins, because paraffins having few side-chains and long carbon chains are urea-adductible<sup>7)</sup>. However, the fraction, which was obtained by treating the urea-adductible paraffins by chromatography with silica gel and then extracting it by pentane, was found to be straight-chain crystalline paraffin. Namely, the micro-paraffin forms micro-crystals, as is shown in Fig. 1, and its

1) B. T. Brooks, C. E. Boord, S. S. Kurtz and L. Schmerling, "The Chemistry of Petroleum Hydrocarbon", Reinhold Publ. Corp., New York (1954).

2) K. Negoro, This Bulletin, 34, 1366 (1961).

3) K. Negoro, *ibid.*, 35, 375 (1962).

4) K. Negoro, *ibid.*, 34, 1374 (1961).

5) A. N. Sachanen, "The Chemical Constituents of Petroleum", Reinhold Publ. Corp., New York (1945), p. 289.

6) W. L. Nelson and L. D. Stewart, *Ind. Eng. Chem.*, 41, 2231 (1949).

7) W. J. Zimmerschied et al., *ibid.*, 42, 1300 (1950).

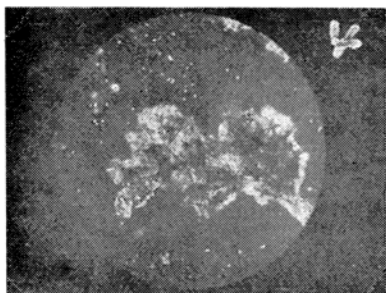


Fig. 1. Micro-crystals of the micro-paraffin.

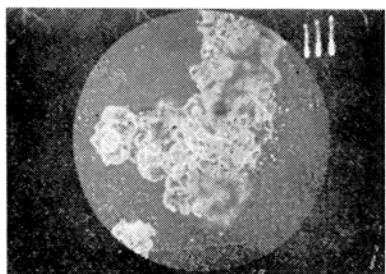


Fig. 2. Crystals of the pentane fraction which had been obtained from the urea-adductible paraffin by chromatography.

X-ray diffraction curve shows that the crystals are imperfect. However, the author recognized that the pentane fraction of the chromatography, with urea-adductible paraffin, formed tabular crystals similar to those of crystalline paraffin and *n*-paraffin<sup>2,8)</sup>, as is shown in Fig. 2, and that the X-ray diffraction pattern was similar to those of crystalline paraffin and *n*-paraffin<sup>3)</sup>.

As described above, a considerable amount of *n*-paraffin was clearly contained in micro-paraffin, and so it is not true that the micro-paraffin is essentially micro-crystallized paraffin with side-chains. The ordinary paraffin waxes consist mainly of *n*-paraffin and contain a small quantity of low melting point hydrocarbons and probably side-chain paraffins<sup>9-12)</sup>.

According to the reports of the compositions of crystalline paraffins obtained by the mass spectrum analysis method<sup>13,14)</sup>, they consist of 80~95% *n*-paraffin, 5~15% isoparaffin, 1~10% cycloparaffin, and 0~0.9% alkylbenzene, though there are small differences corresponding to the sorts of crude oils. On the contrary, studies of the compositions of micro-paraffins have

8) S. Yagi and K. Negoro, *Chem. Ind. (Kagaku Kogyo)*, 8, No. 12, 32 (1957).

9) C. C. Buchler and G. D. Groves, *Ind. Eng. Chem.*, 19, 718 (1927).

10) S. W. Ferris and H. C. Cowles, *ibid.*, 37, 1054 (1945).

11) J. A. Carpenter, *J. Inst. Petroleum Tech.*, 12, 288 (1926).

12) K. Negoro, *Chem. (Kagaku)*, 15, 370 (1960).

13) H. J. O'Neal and T. P. Weir, *Anal. Chem.*, 23, 843 (1951).

14) W. R. Turner, D. S. Brown and D. N. Harrison, *Ind. Eng. Chem.*, 55, 1219 (1955).

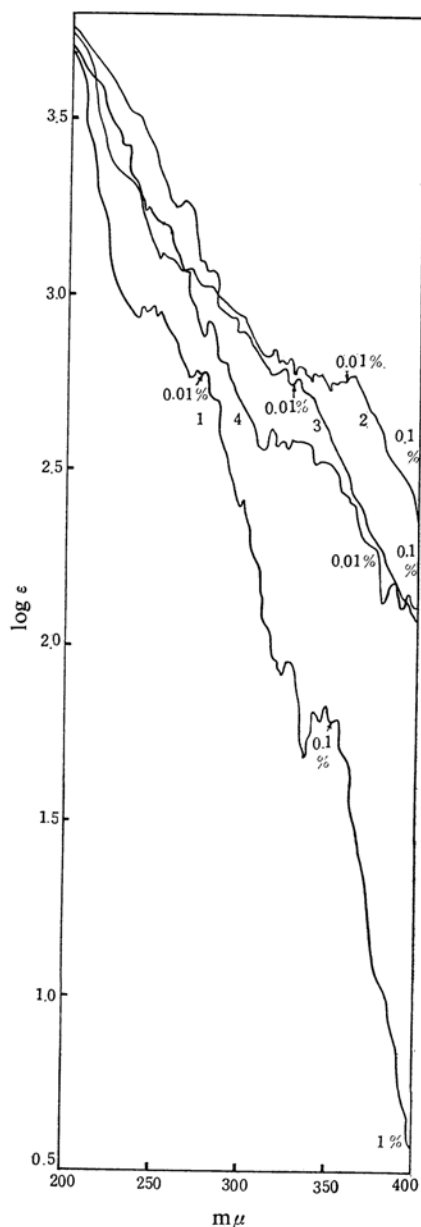


Fig. 5. Ultraviolet spectra of each fraction in asphalt components.

1. Pentane fraction 2. Benzene fraction  
3. Alcohol fraction 4. Residue

very seldom been reported; Ridenour et al.<sup>15)</sup>, however, recently explained that the quantities of urea-adducting material contained in the three sorts of micro-paraffins were 47, 60 and 20% respectively.

The micro-paraffin obtained from the tank residue of Aramco crude oil consisted of various components, as is shown in Table I, and the

15) W. P. Ridenour, I. J. Spinners and P. N. Templin, *TAPPI*, 41, No. 6, 257 (1958).

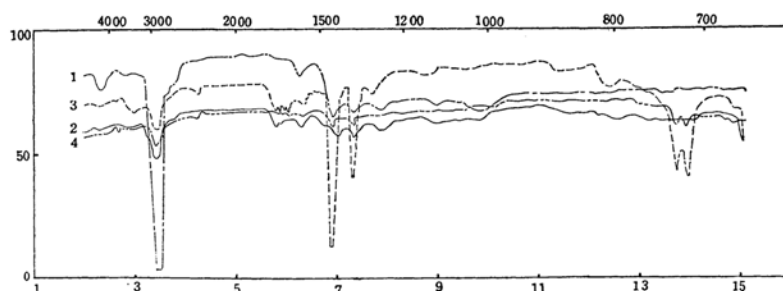


Fig. 4. Infrared spectra of each fraction in asphalt components.

1. Pentane fraction                      2. Benzene fraction  
3. Alcohol fraction                      4. Residue

TABLE I. COMPONENTS OF MICRO-PARAFFINS AND THEIR PROPERTIES<sup>2,3)</sup>

Name	M. p. °C	Refractive index (70°C)	Mean molecular weight	Yield %	Crystal property	Length of carbon chain, Å	Carbon number
Micro-paraffin	73.0	1.4477 <sup>8</sup>	599	—	Micro-crystal	50.8	39
Micro-paraffin (imported)	78.0	1.4442 <sup>85</sup>	581	—	Micro-crystal	53.2	40
Micro-paraffin (de-asphalting)	65.0	1.4406 <sup>75</sup>	583	100.0	Small plate crystal	48.5	37
Micro-paraffin (urea-adducting)	67.0	1.4400	613	61.8	Plate crystal	46.4	35
Micro-paraffin (urea-non-adducting)	54.5	1.4460	620	28.9	Micro-crystal	50.7	39
Urea-adducting micro-paraffin, pentane fraction	65.0	1.4390	607	48.8	Plate crystal	45.9	35
Urea non-adducting micro-paraffin, pentane fraction	54.0	1.4410	636	22.1	Small plate crystal	47.8	36

TABLE II. PROPERTIES OF EACH FRACTION OF THE ASPHALT COMPONENTS

Sample name	Yield, %		Refractive** index	Mean molecular** weight	Crystal property
	vs. Soluble components	vs. Asphalt components			
Pentane fraction	71.8	54.6	1.4685 <sup>70</sup>	593	Plate crystal
Benzene fraction	12.4	9.4	—	564	Amorphous
Alcohol fraction	6.6	5.0	—	571	Amorphous
Residues*	—	24.0	—	599	Amorphous, small plate crystal

\* Pentane insoluble matter of asphalt components.

\*\* Measured by the methods described in a previous report<sup>2)</sup>.

quantity of urea-adductible paraffins which were almost *n*-paraffins was about 60%; furthermore, micro-paraffin showed crystalline properties when isolated by the above treatment.

Clark<sup>16)</sup> has described how hydrocarbons(carbon number 26) having alkyl groups, or a naphthene or benzene ring, etc. at any position of the structure, formed crystals as well as *n*-paraffins. From the above facts, it can be deduced that the peculiar micro-crystallization

of the micro-paraffin is caused by secondary, not essential, factors.

**Micro-crystallizing Substances.**—As has been previously described<sup>2)</sup>, the paraffin formed crystals when asphalt components were removed perfectly from the micro-paraffin by applying the propane de-asphalting method. Therefore, the author considered that original substances for forming fine crystal grains would be present in the asphalt component. Asphalt components form amorphous crystals and are mixtures of various compounds. By chromatography through

16) E. W. Clark, *Ind. Eng. Chem.*, 43, 2526 (1951).

a column packed with alumina gel, the asphalt components were separated into three fractions by being extracted by pentane, benzene and ethyl alcohol. The properties of each fraction were measured, and the results are shown in Table II and in Figs. 3 and 4.

The last absorption band changed to a deep color when the side-chain numbers increased in benzene derivatives. The last absorption band of the asphalt components was  $277\text{ m}\mu$ , which represented a shift of about  $9\text{ m}\mu$  from that of the benzene of no side-chains<sup>17)</sup>, and substances having some side-chains of benzene ring were considered to be present in the asphalt components. Therefore, small amounts of various series of aromatic hydrocarbons besides such benzene derivatives, were also contained in each fraction.

The crystal band was observed at  $723\sim 717\text{ cm}^{-1}$  in the infrared spectrum of the pentane fraction of asphalt components (as has also been found in *n*-dotriacontane or crystalline paraffin). This fraction of asphalt components was almost the same as the ordinary paraffin waxes, and if the fraction was added to crystalline paraffin (m. p.  $53.5^\circ\text{C}$ , mean carbon number 28) or *n*-dotriacontane (m. p.  $69.5^\circ\text{C}$ ,

carbon number 32), micro-crystallization effects could not be observed, as is shown in Figs. 5 and 6\*.

The crystal band was not seen in the infrared spectrum of the benzene-extracted fraction, and it was shown to be amorphous. Therefore, this fraction caused almost no transformation when added to *n*-paraffin.

In the case of an alcohol-extracted fraction, the author discovered that the addition of a small amount of crystalline paraffin formed fine crystal grains, as is shown in Fig. 7; it was also clearly observed, as is shown in Fig.

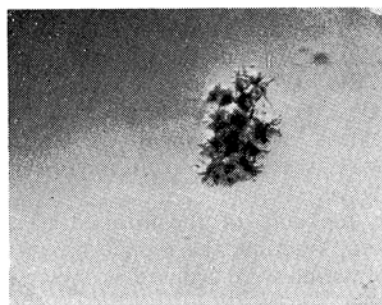


Fig. 7. Transformation of crystals of crystalline paraffin caused by the addition of the alcohol fraction of asphalt components (micro-crystallized).

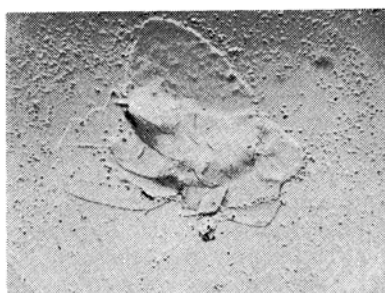


Fig. 5. Transformation of crystals of crystalline paraffin caused by the addition of the pentane fraction of asphalt components (almost no transformation).

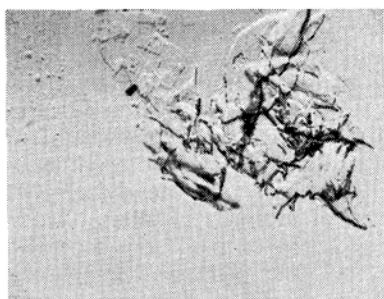


Fig. 6. Transformation of crystals of *n*-dotriacontane caused by the addition of the pentane fraction of asphalt components (almost no transformation).



Fig. 8. Transformation of crystals of *n*-dotriacontane caused by the addition of the alcohol fraction of asphalt components (micro-crystallized).

TABLE III. INFRARED SPECTRUM OF THE ALCOHOL FRACTION OF ASPHALT COMPONENTS

Wave number, $\text{cm}^{-1}$	Assignment of vibration
3410	OH Stretching vibration
2980	C-H Stretching vibration
1731	C=O Stretching vibration
1600	Conjugated double bond stretching vibration
1471	deg-CH Bending vibration
1380	sym-CH Bending vibration
1284~1260	Aromatic derivatives vibration

\* The experiment was made by the method described in a previous report<sup>(4)</sup>, in which the solvent used was purified ethyl alcohol.

17) "Hydrocarbon Chemistry (Tankaisuo Kagaku)", Vol. 2, Kyoritsu Shuppan, Tokyo (1956), p. 69.

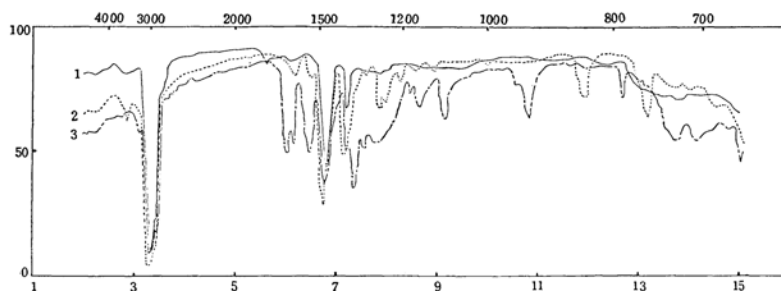


Fig. 9. Infrared spectra of organic compounds.

1. Santopour 2. *p*-Hydroxydiphenyl 3. Picric acid

8, that the fraction caused a remarkable transformation of crystals on *n*-dotriacontane<sup>19</sup>, on which the asphalt components themselves had almost no noticeable effects. Therefore, the residues of the asphalt components were recognized as showing small micro-crystallization effects.

From the data of the infrared spectrum of the alcohol fraction, the atomic groups present in the fraction were deduced as shown in Table III.

The absorption band which originated in hydroxyl groups at  $3410\text{ cm}^{-1}$  was remarkably attractive. As has previously been described<sup>42</sup>, the infrared spectra of Santopour, picric acid, and *p*-hydroxydiphenyl formed fine crystal grains of crystalline paraffin or *n*-dotriacontane, as is shown in Fig. 9. In each spectrum, however, the absorption band originating in the carboxyl groups was seen at  $3190\sim 3520\text{ cm}^{-1}$ .

The shape of the above curves of the spectra was very similar to the curves of the spectra of the alcohol fraction of the asphalt components. The infrared spectra of Santopour and those of the alcohol fraction of the asphalt components (in the whole sphere) were very similar, and it was concluded that their structures were similar, too.

Santopour has been reported to be 2,3,5,6-tetraalkylbenzene<sup>18</sup>, CC1=CC(C)C(C)C=C1 and its mean

molecular weight was measured to be 265. The alkyl chains at the 4 radicals of the benzene ring were therefore considered to consist of  $\text{C}_4$ .

If the alcohol-extracted fraction, isolated from the asphalt components, had a structure like Santopour, the length of the methylene chain was presumed to be  $\text{C}_{34}$ , because its molecular weight was 571. Therefore, the alcohol fraction was considered to have parts of alkyl chains much longer than Santopour.

It is noticeable that the formation of fine

crystal grains of paraffin is caused in the presence of the compounds of similar structures having hydroxyl groups and benzene rings.

**Crystal Structure of the Micro-paraffin.**—Many studies have been made on the crystals of *n*-paraffin<sup>19-23</sup>; its unit cell has been reported to form hexagonal, orthorhombic, monoclinic, or triclinic system, according to the sort of individual hydrocarbons and the temperature. As has been mentioned above<sup>3</sup>, the crystal systems of paraffin waxes and micro-paraffins were orthorhombic.

The values of  $d_{110}$  and  $d_{200}$ , the length of the *a* and *b* axis, the cross-sectional area occupied by one molecule, and the molecular volume were calculated; the results are shown in Table IV.

The above values on crystal lattice are mean values, because micro-paraffin is a mixture of various hydrocarbons. The tips of carbon chains are not arranged in order. It seems to be reasonable to consider that its lattice spacings are somewhat larger than those of *n*-paraffin and that its side-chains are seen at some places of the paraffin chains. In particular, the values of both  $d_{110}$  and  $d_{200}$  of the urea non-adducting paraffins, isolated from the micro-paraffin by the urea method, were so large that it was proved to have many side-chains.

According to Edwards<sup>24</sup>, the development of crystal lattice was affected by the molecular weights of hydrocarbons and by the presence of non-*n*-hydrocarbons. The mean carbon chain of micro-paraffins was somewhat longer than that of ordinary crystalline paraffins, and the molecular volume was nearly 20~30% larger than that of ordinary paraffins.

Several peaks of the X-ray diffraction curve of 001, 002, etc. were seen in the case of the crystalline paraffin of *n*-dotriacontane, but the

18) N. Iimure, "Guide-Book of Petroleum Products (Sekiyu Seihin Gaido Bukku)", Sangyo Tosho, Tokyo (1956), p. 162.

19) A. Müller, *Proc. Roy. Soc.*, **A120**, 437 (1928).

20) A. Müller, *ibid.*, **A127**, 417 (1930).

21) A. Müller, *ibid.*, **A138**, 514 (1932).

22) C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).

23) A. E. Smith, *J. Chem. Phys.*, **21**, 2229 (1953).

24) R. T. Edwards, *TAPPI*, **41**, No. 6, 267 (1958).

TABLE IV. RESULTS OF X-RAY DIFFRACTION FOR VARIOUS PARAFFINS<sup>3)</sup>

Sample name	$d_{110}$ , Å	$d_{200}$ , Å	a Axis, Å	b Axis, Å	Cross-sectional area, $\times 10^{-16}$ cm <sup>2</sup>	Molecular vol. Å <sup>3</sup> /mol.
Crystalline paraffin (m. p. 53.5°C)	4.19	3.78	7.54	5.03	19.0	708
Micro-paraffin	4.16	3.75	7.50	5.01	18.8	955
Micro-paraffin (de-asphalting)	4.16	3.76	7.52	5.00	18.8	911
Micro-paraffin (Shell)	4.16	3.75	7.50	5.01	18.8	928
Micro-paraffin (commercial)	4.16	3.75	7.50	5.01	18.8	998
Micro-paraffin, urea-adducting paraffin	4.16	3.76	7.52	5.00	18.8	872
Micro-paraffin, urea non-adducting paraffin	4.21	3.80	7.60	5.05	19.2	974
Micro-paraffin pentane fraction	4.20	3.79	7.56	5.04	19.0	900
Urea-adducting micro-paraffin, pentane fraction	4.16	3.75	7.50	5.01	18.8	867
Urea non-adducting micro-paraffin, pentane fraction	4.20	3.79	7.56	5.04	19.0	909
<i>n</i> -Dotriacontane	4.15	3.77	7.54	5.03	19.0	804

peak was only one in the case of the micro-paraffin<sup>3)</sup>. Moreover, the peaks of less than 002 in the urea-adducting materials of micro-paraffin and its pentane-extracted fraction revealed that their crystal structures resembled those of *n*-paraffin. This presumption was verified by observation of the crystal structure of paraffins traced on a carbon film with an electron microscope by applying the replica method<sup>25,26)</sup>.

**Micro-crystallization Phenomenon.**—A few reports have been made on the spiral growth of the crystal of *n*-paraffin<sup>27-29)</sup>; it was studied by the present author<sup>8)</sup> and also by Jaccordine<sup>30)</sup> with a phase-contrast microscope on paraffin crystals. Asphalts resins or dark color substances, etc. in petroleum inhibited the crystallization of paraffins<sup>31)</sup> in the case of ordinary paraffin waxes, and very slight dust particles prevented the grow-step of the crystal growth<sup>29)</sup> in the studies of the spiral growth.

The author has already reported several phenomena revealing that the formation of fine crystal grains of micro-paraffin is caused by secondary factors<sup>2-4,32)</sup> and has discussed the cause of the micro-crystallization phenomena.

The relation between the concentration of Santopour, picric acid, *p*-hydroxybiphenyl, and the alcohol fraction of asphalt components and  $\log \epsilon$  at each wavelength are shown in the graphs. Therefore, 10 mg. of each organic compound was added to 100 mg. of the crystalline paraffin or *n*-paraffin to crystallize, and the mother liquor was taken out to measure the  $\log \epsilon$ , which was plotted in the above graphs for investigation. However, the amount of each organic compound in the liquor was discovered to be not very different from that previously added, even taking into consideration the effects of the presence of paraffin on the  $\log \epsilon$ . Accordingly, it may be surmised that very few compounds are contained in the crystal lattice of paraffin.

Moreover, the amount of crystallized paraffin was weighed, and the crystal growth of 100 mg. of the crystalline paraffin (m. p. 53.5°C) was inhibited by the presence of such organic compounds; the non-crystallized amounts have been calculated and are shown in Table V.

TABLE V. CHANGE IN AMOUNTS OF THE PARAFFIN CRYSTAL CAUSED BY SOME SORTS OF ORGANIC COMPOUNDS

Name of Compounds	Crystallized amount, mg.	Non-crystallized amount, mg.
—	94.1	5.9
Picric acid	69.9	30.1
Santopour	67.2	32.8
<i>p</i> -Hydroxydiphenyl	66.2	33.8
Alcohol fraction of asphalt components	64.5	35.5

25) K. Negoro, *Science (Kagaku)*, **31**, 326 (1961).26) K. Negoro, on application to *J. Japan Petroleum Inst. (Sekiyu Gakkaishi)*.27) I. M. Dawson and V. Vand, *Nature*, **167**, 476 (1951).28) I. M. Dawson and V. Vand, *Proc. Roy. Soc.*, **A206**, 555 (1951).29) N. G. Anderson and I. M. Dawson, *ibid.*, **A218**, 255 (1953).30) R. J. Jaccordine, *Nature*, **187**, 498 (1960).31) N. F. Chamberlin, G. A. Dinouddie and J. L. Franklin, *Ind. Eng. Chem.*, **41**, 566 (1949).32) K. Negoro, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **64**, 295 (1961).

It was made clear by those results that the crystallization of the paraffin was fairly much inhibited by the presence of such organic compounds. As has been described previously, micro-paraffin contained more side-chain components than the crystalline paraffin; therefore, its crystal growth was more prevented, and its tendency to inhibit crystallization was larger than that of crystalline paraffin. Accordingly, it seems reasonable to consider that the formation of fine crystal grains of micro-paraffin is made possible by the presence of the alcohol fraction, which has been separated from micro-paraffin materials and which is supposed to have a structure consisting of an alkyl chain and a benzene ring with hydroxyl groups.

The compounds with a similar structure wrap up the paraffin molecules in the crystallization of paraffin and inhibit the formation of the crystal lattices by a continuous arrangement of paraffin molecules to form larger crystals. As a result, the crystallization is partially prevented, and the formation of fine crystal grains occurs. Very small tabular crystals are also rolled up to form needle crystals, by which the direction perpendicular to the 110° side agrees with the length for the smaller surface area and the more stable form before the crystals grow up in the direction of a and b axes.

### Experimental

**Chromatography.**—Fifty grams of an asphalt component isolated from the tank residues of Arabian crude oil (Aramco oil of Saudi-Arabia)<sup>32</sup> was extracted by a Soxhlet extractor at 50–60°C with 1 l. of purified benzene (b. p. 50–60°C) for about 10 hr. The benzene-extracted components were isolated from the insoluble components by filtration. The yields were 39 and 12 g. respectively. The system for chromatography consisted of 5 columns 100 cm. long and 2 cm. in diameter and of 5 columns 75 cm. long and 1.5 cm. in diameter; all the columns were packed with 1.6 kg. of 200 mesh alumina gel (a product for chromatography, manufactured by the Kanto Kagaku Co.). Then, the benzene-extracted-components solution was poured into the top of the first column. The refractive index of the elute solution showed a larger value than that of benzene. Then the solution was poured into the second column. The index was examined successively at each column, and the last index agreed with that of benzene. Then it was extracted by 52 l. of pentane (b. p. 40–50°C), 67 l. of purified benzene (b. p. 80°C), and 42 l. of purified ethyl alcohol (b. p. 78°C), successively and classified into its extracted fractions. In this case, the index of each solvent had been measured previously; as well, each index of each elute solution was examined. It was extracted by the same solvents (pentane, benzene and ethyl alcohol) until the latter value agreed with the former. Then, each extracted

fraction was obtained by using the above amounts of the solvents.

**X-Ray Diffraction and Absorption Spectra.**—A X-ray diffractometer (Geiger flex, manufactured by the Rigaku Denki Co.) was used for the measurement of the X-ray diffraction<sup>33</sup>. The samples were fixed on glass, and the measurements were made in the range of 0°–90° of  $2\theta$  (scanning speed, 1 deg./min.) and 25–31° (scanning speed, 1/4 deg./min.) with  $\text{FeK}\alpha$ , and in the range of 0–5° (scanning speed, 1 deg./min.) with  $\text{CuK}\alpha$ .

As has already been reported<sup>32</sup>, the sample solution of purified *n*-hexadecane was prepared by the weighing method, and a photo-electric spectrophotometer of type EPU-2 (manufactured by the Hitachi Mfg. Co.) was used for the measurement of the ultraviolet spectrum. An infrared spectrophotometer (Perkin Elmer Model-21) with a sodium chloride prism was used for the measurement of the infrared spectrum. As has previously been reported<sup>32</sup>, each sample of the various paraffins or the asphalt components was applied to the spectrophotometer for measuring. However, organic compounds were measured by the Nujol method with purified liquid paraffin.

**Action of Various Organic Compounds (Table V).**—10, 5 and 1 mg. each of Santopour, picric acid, *p*-hydroxydiphenyl, and the alcohol fraction of the asphalt components were weighed out and dissolved in 25 ml. of purified ethyl alcohol, which had been confirmed as suitable for use as a diluent by the measurement of the ultraviolet spectrum in the range of 200–400  $\text{m}\mu$ .

Each amount was diluted with ethyl alcohol to the constant ratio (*p*-hydroxybiphenyl 0.001 wt. %, and the others 0.01 wt. %), and the absorptions at each wavelength (Santopour, 264  $\text{m}\mu$ ; picric acid, 270  $\text{m}\mu$ ; *p*-hydroxydiphenyl, 256  $\text{m}\mu$ ; the alcohol fraction of asphalt components, 277  $\text{m}\mu$ ), which had been selected according to the results of the ultraviolet spectrum of each organic compound measured previously, were measured to determine  $\epsilon$ . The relation between the concentration and  $\epsilon$  is shown in the graph. One hundred milligrams of the crystalline paraffin (m. p. 53.5°C; mean carbon number, 28) was weighed in an Erlenmeyer flask with a stopper, and 10 mg. of each of the various organic compounds described above was added to the flask to be treated<sup>34</sup>. The crystallized paraffins were isolated by filtration and dried at below 30°C until reaching a constant weight, which was measured to compute the amount of non-crystallized paraffins. Then, the absorption at respective constant wavelengths was measured to compute for each filtrate, and each content of organic compounds was determined.

### Summary

1) The micro-paraffin has longer mean carbon chains than those of ordinary crystalline paraffins, and the content of side-chain hydrocarbons is less than that in ordinary paraffins; its crystals belong to an orthorhombic system, and the formation of fine crystal grains is a result of secondary causes.

2) If the paraffin is recrystallized in ethyl alcohol in the presence of organic compounds of a similar structure which have benzene rings with hydroxyl groups such as Santopour, picric acid, *p*-hydroxybiphenyl, etc., the crystal growth is inhibited and the crystallized amount of the paraffin crystals is reduced, which is the cause of the formation of fine crystal grains.

3) The alcohol-extracted fraction, isolated from the micro-paraffin materials, has a fairly long alkyl chain and benzene rings with the hydroxyl groups. The crystalline or *n*-paraffin is micro-crystallized, the same as the above organic compounds, when a very small amount of the fraction is added to it.

4) The content of *n*-paraffin in the micro-paraffin is less than that in ordinary crystalline paraffin, but the former contains more side-chain components. The paraffin forms fine crystal grains in the presence of compounds such as the alcohol-extracted fraction.

5) As a result of the purification by the urea method and chromatography, X-ray diffraction, etc., a considerable amount of the crystalline *n*-paraffins has clearly been found to be contained in micro-paraffin. Therefore, the micro-paraffin does not consist of side-chain paraffin and is not originally micro-crystallized, as has hitherto been believed.

6) The effects of such additive organic compounds on *n*-dotriacontane, on crystalline paraffins or on a mixture of various hydrocarbons are not the same. In the case of the latter, the tips of the carbon chain in the

crystal lattice are arranged in disorder, with a few side-chains; therefore, the crystal growth of the paraffin is believed to be inhibited and then the formation of fine crystal grains occurs.

7) The additive organic compounds wrap up paraffin molecules in the crystallization of paraffin, and the process from the formation of the crystal lattices to the growth of large crystals is so inhibited that the crystal growth is prevented. Crystallization seems to be partially prevented, and micro-crystallization or needle crystallization of small tabular crystals occurs.

The author wishes to express his deep appreciation to Professor Ryoza Goto and Professor Saburo Yagi, Kyoto University, for their cordial guidance and discussion throughout this research; he also is grateful to Dr. Kenziro Asai and Dr. Tsuneo Seto, Kyoto University, for their cordial guidance in the analyses of X-ray diffraction, and to Mr. Kazuo Naito and Mr. Osamu Nanbu, Osaka Ind. Tech. Lab., who co-operated in the infrared spectrum experiments. He also wishes to thank Mr. Takashi Matsuoka and the personnel of the Central Research Lab. of Nippon Mining Co., for their co-operation in the measurement of the X-ray diffraction and to all the other personnel of Nippon Mining Co. for their great kindness throughout this research.

Central Research Laboratory  
Nippon Mining Co.  
Kitaadachi-gun, Saitama