Studies on Micro-paraffin. IV. On the Transformation of Paraffin Crystal by Addition of Pure Substances

By Kazuo NEGORO

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Numerous phenomena, concerning the micro-crystallization of microparaffin derived by secondary cause, were previously reported[1]. Many investigations were made for the crystal growth of paraffin wax in the field of lubricating oils, because it was supposed to have great effects on the pour points of oils[2]. The pour points of lubricating oils are not the melting points of oils, but it seems to be reasonable to consider that the pouring phenomenon happens when the whole fluidity of lubricating oils is lost by the crystallization of wax components contained in the oils. Therefore, additional agents are used for pour point depressants to keep the fluidity of lubricating oils in low temperature inhibiting the crystal growth of paraffin waxes. They are supposed to inhibit the crystal growth of paraffin waxes, because they are adsorbed by paraffin waxes rather than oils.

The addition of any inorganic and organic substances to ordinary crystalline paraffin waxes were examined and their structure which should inhibit the crystal growth of paraffin waxes. In particular, as seen in the report[3], the cause of micro-crystallization of microparaffins was considered to be affected by substance with hydroxyl groups derived by the results of studies on ultraviolet and infrared spectra, etc. of the components separated from the microparaffin by a propane deasphalting method, urea adducts method, and chromatography: hence, the behavior of various organic compounds having OH groups should be noticed. Then, many pour point depressants for lubricating oils, additional agents to paraffin waxes[4], and direct dyes[5] were examined at the same time. Furthermore, pure organic substances considered to be effective for the crystal growth of paraffin waxes were studied at the base of pure *n*-dotriacontane (forming plate crystals), and their effects on crystal growth of *n*-hydrocarbon (simple substance, but not mixture) were investigated.

As the above results, such as Santopour or pour point depressants for lubricating oils, picric acid, *p*-hydroxydiphenyl, and some direct

1) K. Negoro, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 64, 295 (1961).
2) K. Horiguchi, "Junkatsuyu Kagaku" (The Chemistry of Lubricating Oils), Sankyo, Tokyo (1958), p. 295.
3) K. Negoro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippn Kagaku Zasshi*), 82, 229 (1961).
4) K. Negoro, *Oil Chemistry* (*Yukagaku*), 7, 23 (1958).
5) S. Inokawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 76, 726 (1955).

dyes were found to be the substances affected on the transformation of crystal growth of paraffins.

These behaviors shall be cleared by future studies, they are now being investigated by X-ray diffraction, and infrared spectra of microparaffins. However, it is very interesting that the existence of the above organic substances with hydroxyl groups and similar molecular structure, affects the transformation of the crystal of paraffin waxes. It was found, also, that there was a difference between the paraffin waxes (mixture of various hydrocarbons) and *n*-dotriacontane for such effects of addition. Therefore, the composition of paraffin was considered to be effective for the micro-crystallization of microparaffins.

Experimental

Materials.—*Crystalline Paraffin.*—The sample of wax was made in the Funakawa Refinery, Nippon Mining Co., m. p. 53.5°C, and refractive index $1.4308^{70.0}$.

n-Dotriacontane.—The product of Fischer Scientific Co., and purchased from Pacific Gulf Oil Co.,[6] m. p. 69.2°C, sp. gr. $0.7831^{70.0}$, and refractive index $1.4308^{70.1}$.

n-Dotriacontane was of a high purity, but a content of some impurities was recognized by the result of the ultraviolet spectrum (wavelength 220~400 mμ) measurement with purified *n*-hexadecane as diluent. Accordingly, purification was conducted with 10% of activated clay at 75°C (yield of 78%). Such purified *n*-dotriacontane was confirmed to contain no impurities by a measurement of the ultraviolet spectrum as above, m. p. 69.5°C and refractive index $1.4315^{73.0}$.

The above values were confirmed to be almost equal to those in the literature[7].

Chemicals.—Many inorganic and organic chemicals, added to the crystalline paraffin or *n*-dotriacontane, were of special or 1st grade made by Kanto Kagaku Co.

Solvents.—Ethyl alcohol was purified by a general method[8], and its boiling point was 78.0°C.

Crystallization.—Crystalline paraffin or *n*-dotriacontane was weighed accurately on a chemical balance; and 10, 1 and 0.1 wt.% of each inorganic or organic chemicals (as additive) were also weighed accurately. Both the paraffin and the additive were placed in an Erlenmeyer's flask and melted at 80°C in a thermostat. Even when there were some chemicals not melted at 80°C, the next operation was started; 1 g. of purified ethyl alcohol was added to 300 cc. of each sample with a pipette, and was warmed at 75±1°C in the thermostat to make the sample soluble in ethyl alcohol with intermittent stirring. Then, it was gradually cooled to room temperature for the growth of the crystal of the paraffin.

Observation of Crystals by Microscope[9].—The crystal of each sample was placed on a slide glass with a syringe, and was observed with an ordinary or phase-contrast microscope; and then, photographs of the state of each crystal were taken.

Results and Discussion

Effects of Various Substances on Crystallization of Crystalline Paraffin.—*Effects of Inorganic Substances.*—The effects of the existence of various inorganic substances on the crystallization of crystalline paraffin were investigated. The crystalline paraffin at the base forms thin and large plate crystals as shown in Fig. 1, which mainly consists of *n*-paraffin (containing 88~90% of the straight chain adductible paraffin), and it is supposed that the average number of carbon chains of hydrocarbons contained to be 27*[1].

×225

Fig. 1. Crystals of crystalline paraffin.

In the case of each 10% of various metals, oxides, acids, alkalis, salts, etc., such as sulfur, zinc powder, manganese dioxide, silica, zinc oxide, aluminum chloride, sodium bicarbonate, potassium chlorate, alum, silver nitrate, ammonium vanadate, sulfuric acid, hydrochloric acid, sodium hydroxide, etc., existed with crystalline paraffin, no transformation were observed in the crystallization of the crystalline paraffins.

Effects of Organic Substances.—Next, the effects of 0.1~10% of various pure organic substances on crystalline paraffin were also examined. Experiments were conducted on various organic compounds; and at the same time, as explained above by the investigation of the crystal properties[1,3], ultraviolet spectra and infrared spectra on each fraction of microparaffin separated by the application of propane deasphalting method, urea adducts method, chromatography etc., the compound with hydoroxyl or carbonyl groups was considered

6) Personal communication from H. I. Goodman (Pacific Gulf Oil Co.).

7) F. Francis, O. M. Watkins and R. W. Wallington, *J. Chem. Soc.*, **121**, 1529 (1922).

8) "Text-book on Chemical Experiments" (Jikken Kagaku Koza), 2 (Fundamental Technique II), Maruzen, Tokyo (1956), p. 78.

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

*1 It is presumed by X-ray diffraction method (X-ray diffraction of various paraffins will be mentioned in the later report of this series to be continued).

TABLE I. EFFECTS OF ORGANIC SUBSTANCES ON THE CRYSTALLIZATION OF PARAFFIN

Sample	Molecular formula	M. p.*1	Solubility in alcohol*2	Effects on crystallization of paraffin
p-Hydroxydiphenyl	$C_6H_5C_6H_4OH$	161.5	Sol.	Transformation (micro-crystallization)
Picric acid	$HOC_6H_2(NO_2)_3$	118	Sol.	Transformation (micro-crystallization)
Glucose	$C_6H_{12}O_6$	134	Sol.	Transformation
Quinizarine	$C_6H_4\langle^{CO}_{CO}\rangle C_6H_2(OH)_2$	177.5	Sol.	Transformation (micro-crystallization)
Calcium stearate	$(C_{17}H_{35}COO)_2Ca$	110~115	Insol.	Transformation
Barium stearate	$(C_{17}H_{35}COO)_2Ba$	195~200	Insol.	Transformation
Aluminum stearate	$(C_{17}H_{35}COO)_3Al$	118~120	Insol.	Transformation
Zinc naphthate	$(C_6H_{11}COO)_2Zn$		Sol.	Transformation
Lead naphthate	$(C_6H_{11}COO)_2Pb$		Sol.	Transformation

*1 Melting point measured by the capillary tube method.
*2 Sol, soluble Insol, insoluble

to give effects on the micro-crystallization of microparaffin. Under the above circumstances, in particular, the various types of organic compounds with functional groups such as hydroxyl or carbonyl group were examined in a wide scope. In the case of each 10% of various aromatics, alcohols, aldehydes, ketones, acids, esters, salts, phenols, amines, nitrogen compounds, sulfur compounds, etc., such as naphthalene, *tert*-butyl alcohol, cetyl alcohol, cholesterol, phenol, α- and β-naphthol, resorcinol, glycerine, pyrogallol, *p*-hydroxydiphenyl, picric acid, *m*- and *p*-nitrophenol, *o*-, *m*- and *p*-dinitrobenzene, aniline, lauril amine, triethanolamine, phenylhydrazine, azobenzene, methyl orange, hydroxyazobenzene, dinitrophenyl hydrazine, benzaldehyde, glucose, methylisobutyl ketone, acetophenone, α- and β-naphthoquinone, quinizarine, benzoic acid, acetic acid, naphthenic acid, oleic acid, stearic acid, oxalic acid, adipic acid, 2.3- and 2.5-dihydroxybenzoic acid, salicylic acid, calcium acetate, calcium, barium and aluminum stearate, lead oleate, zinc and lead naphthate, amyl acetate benzyl acetate, ethyl chloride, trichloroethylene, methylchlorostearate, *n*-heptyl mercaptane, dibenzyl disulfide, etc. exist with crystalline paraffin, were observed in the crystallization of the crystalline paraffin, were observed in the crystallization of the crystalline paraffins. Each of the various organic compounds which transformed the crystalline properties of paraffin when being added to it, are shown in Table I.

The substances having hydroxyl groups combined with an alkyl group or a benzene ring, were hardly affected on crystallization of paraffins. Glycerine, ethylene glycol, pyrogallol, etc.[2] which were said to drop the pour points of lubricating oils when being added, were not much affected on the crystal growth of paraffins. However, in the case of *p*-hydroxydiphenyl and picric acid, the crystal growth of crystalline paraffins was evidently inhibited as shown in Figs. 2 and 3, respectively, and it is very interesting that they show a microcrystalline state.

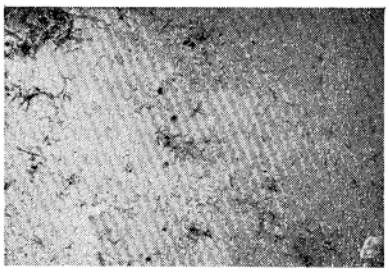
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Fig. 2. Transformation of crystals of crystalline paraffin caused by the addition of *p*-hydroxydiphenyl.

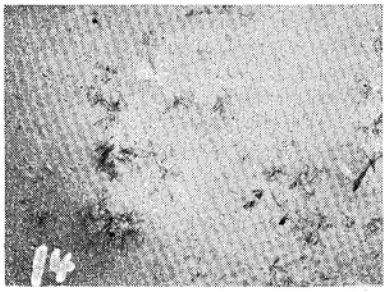
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Fig. 3. Transformation of crystals of crystalline paraffin caused by the addition of picric acid.

In the next stage, nitrogen compounds such as compounds having nitro, amino or azo groups, etc. were examined. But almost no effects were observed on such compounds as shown above. As the results of investigations on the compounds having aldehyde or ketone groups, quinizarine (having two hydroxyl groups in addition to ketone groups and

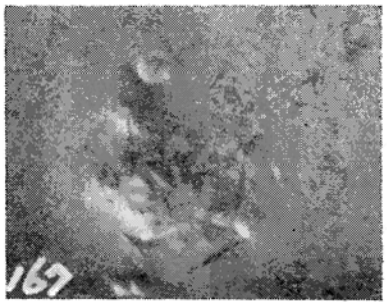
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Fig. 4. Transformation of crystals of crystalline paraffin caused by the addition of quinizarine.

benzene nucleus) formed the microcrystallization of crystalline wax as shown in Fig. 4. Almost no effects were given by various types of organic acids having hydroxyl groups. However, in the presence of metallic salts of stearic or naphthenic acid, microcrystalline crystals were found accompanied by plate crystals of crystalline paraffin. The metallic soaps of fatty acids are used for the pour point depressant of lubricating oils[10], and they are said to have larger effects when their molecular weights are larger. For instance, the effects of the existence of metallic salts of stearic and naphthenic acids on the crystals of a crystalline paraffin are shown in Figs. 5 and 6, respectively.


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Fig. 5. Transformation of crystals of crystalline paraffin caused by the addition of calcium stearate.

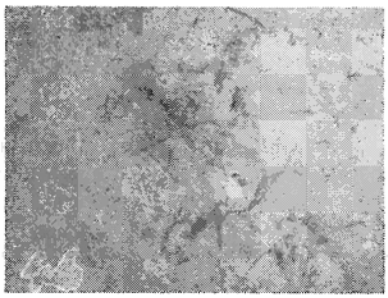
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Fig. 6. Transformation of crystals of crystalline paraffin caused by the addition of zinc naphthate.

10) Y. Tanaka, R. Kobayashi and T. Tsukuda, *J. Soc. Chem. Ind. Japan* (*Kôgyô Kwagaku Zassi*) **38**, 10, 28, 1033 (1935).

Though effects of the addition of a few compounds of sulfur were investigated, so far, substances inhibiting the crystal growth of crystalline paraffins have not been found.

The substances giving effects on the transformation of crystallization are shown in Table I.

Effects of Addition Agents.—The results of the investigations on addition agents of paraffin waxes had been already reported[11]. The effects of the existence of such agents on the crystals of paraffin waxes were examined. Also the pour point depressants, recently being in practical use in the field of lubricating oils, are considered to have effects on keeping the fluidity of lubricating oil in lower temperature[2] by inhibiting the growth of paraffin crystals mixed in oils. Then, the effects of depressants on sale upon the crystallization of crystalline paraffins when mixed in the paraffins were also examined as above, and the results are shown in Table II.

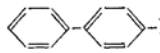
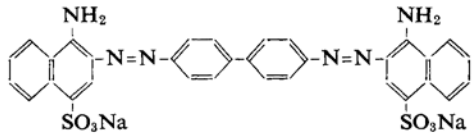
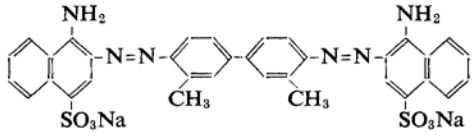
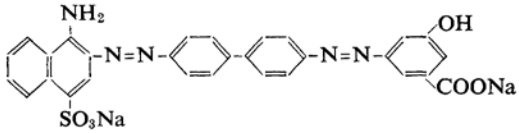
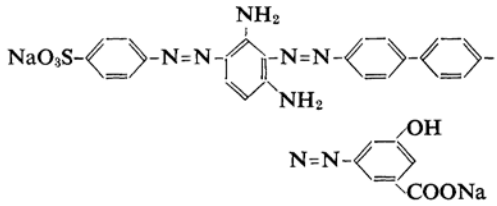
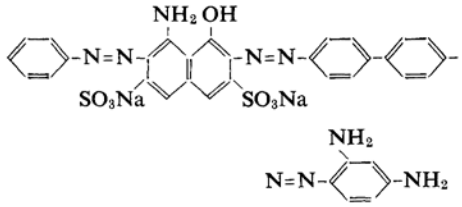
It was found that the substance, having the most remarkable effect on the change of the crystals of paraffin wax, was Santopour. In

Table II. Effects of addition agents on the crystallization of paraffin

Sample	Effects on crystallization of paraffins	Summary
Polyethylene	no	Improver of m. p., which micronizes the structure of paraffin
Acra wax c	no	Synthetic paraffin. Improver of m. p.
Carbo wax	no	Poly (ethylene glycol) (mol. wt. 4000)
Vistac	no	Polybutene (mol. wt. 1100 and 3400)
Ar wax	no	Paraffin added by polyethylene
Stroba wax	no	Paraffin mixed with a small quantity of resin
Adva wax	Somewhat transformation	Microparaffin added by polyethylene
Chloro-naphthalene	Transformation	Chlorinated naphthalene
Santopoid 23RI	no	Addition agents of lubricating oils
Ionol	no	Addition agents of lubricating oils
Santopour	Transformation (micro-crystallization)	Addition agents of lubricating oils
Santolube 70	no	Addition agents of lubricating oils

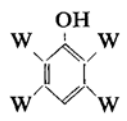
11) K. Negoro, *Oil Chemistry* (*Yukagaku*), **7**, 97 (1958).

Table III. Effect of direct dyes

Sample	Structural formula	Effects on crystallization of paraffin
p-Aminodiphenyl		no
Congo red		no
Benzopurprine		no
Nippon green B conc.		Transformation (micro-crystallization)
Nippon orange R		Transformation
Nippon brown 3G		Transformation
Nippon dark green B conc.		Transformation
Nippon deep black ex. conc.		Transformation

this case, the phenomenon of micro-crystallization as picric acid, *p*-hydroxydiphenyl, etc. was confirmed by microscopy as shown in Fig. 7.

Santopour is the product made from phenol and paraffin wax[12], and it is said to form the following structure. It is attractive that the structure is similar to that of picric acid which caused the crystals of the crystalline paraffins to micro-crystallize.



(W; paraffinic chain)

Chloronaphthalene*, which was made by blowing chlorine into naphthalene, was added to the crystalline paraffin. Then, the crystal growth of paraffin was inhibited, and almost no crystal of paraffin appeared by cooling under the same condition; it was attractive

12) N. Iimure, "Guide-book of Petroleum Products", Sangyo Tosho, Tokyo (1956), p. 162.

* The trial product by K. Hashizume (Fukushima Paraffin Paper Co.), was used and its composition is obscure.

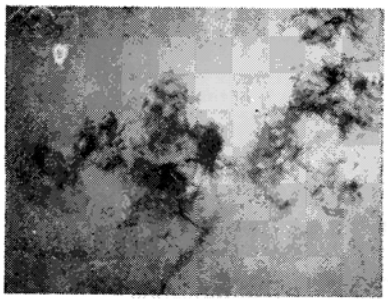

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Fig. 7. Transformation of crystals of crystalline paraffin caused by the addition of Santopour.

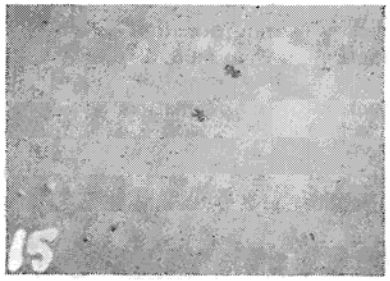
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Fig. 8. Transformation of crystals of crystalline paraffin caused by the addition of chloronaphthalene.

that only a small amount of amorphous crystals was observed as shown in Fig. 8.

Effects of Direct Dyes.—It has been reported[5] that the direct dyes having functional groups such as hydroxyl group, amino group, etc. made the gelatin of methyl cellulose by bridge-making through each molecule. Then, the effects of such dyes on crystal growth of the paraffin were examined. The results of experiments on 9 sorts of dyes are shown in Table III.

It is very interesting that in the case of direct dyes also, only the compounds having hydroxyl groups gave effects on crystal growth of the crystalline paraffin.

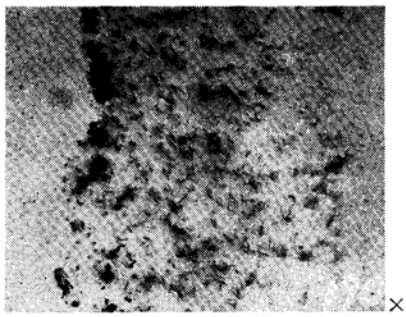
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Fig. 9. Transformation of crystals of crystalline paraffin caused by the addition of Nippon green B conc.

Effects of Asphalt Components.—Similarly, the asphalt component separated from heavy oil containing microparaffin[1] by propane deasphalting method was added to the crystalline paraffin. Then, the crystals of the paraffin were microcrystallized as shown in Fig. 10, and it was interesting that the micro-crystalline state was very closely similar to that caused by the addition of Santopour, picric acid, *p*-hydroxydiphenyl, etc.

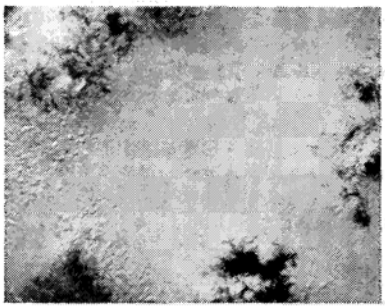
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Fig. 10. Transformation of crystals of crystalline paraffin caused by the addition of asphalt component.

Effects of Various Substances on Crystallization of *n*-Dotriacontane.—Each of the various organic compounds which transformed the crystalline properties of paraffin when being added to it, were added to a purified *n*-dotriacontane (formed thin plate crystals as shown in Fig. 11) as the above examination. Then, its effects on the crystallization of *n*-dotriacontane were investigated. These results are shown in Table IV.

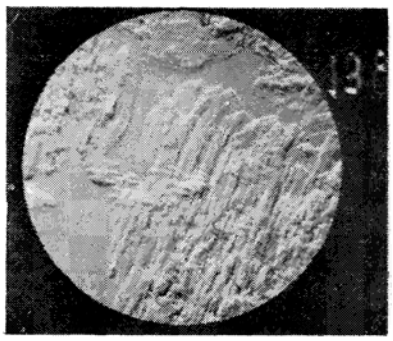
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Fig. 11. The crystals of *n*-dotriacontane.

The phenomena of micro-crystallization which gave effects on the crystal when *p*-hydroxydiphenyl or picric acid was added to *n*-dotriacontane are in Figs. 12 and 13, respectively. Figure 14 shows the photograph of crystal transformations of *n*-dotriacontane when Santopour, addition agent of lubricating oils, was added to it, and it is easy to find out crystals of needles.

Table IV. Effects of various organic substances on the crystallization of *n*-dotriacontane

Sample	Effects on crystallization of *n*-dotriacontane	Sample	Effects on crystallization of *n*-dotriacontane
p-Hydroxydiphenyl	Transformation (micro-crystallization)	Adva wax	Almost no transformation
Picric acid	Transformation (micro-crystallization)	Santopour	Transformation (micro-crystallization)
Glucose	Almost no transformation	Nippon green B conc.	Transformation
Quinizarine	Almost no transformation	Nippon orange R	Almost no transformation
Calcium stearate	Almost no transformation	Nippon brown 3G	Almost no transformation
Barium stearate	Almost no transformation	Nippon dark green B conc.	Almost no transformation
Aluminum stearate	Almost no transformation	Nippon deep black ex. conc.	Almost no transformation
Zinc naphthate	Almost no transformation	Chloronaphthalene	Almost no transformation
Lead naphthate	Almost no transformation	Asphalt component	Transformation

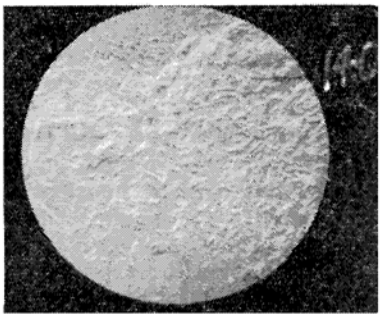

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Fig. 12. Transformation of crystals of *n*-dotriacontane caused by the addition of *p*-hydroxydiphenyl (micro-crystallized).

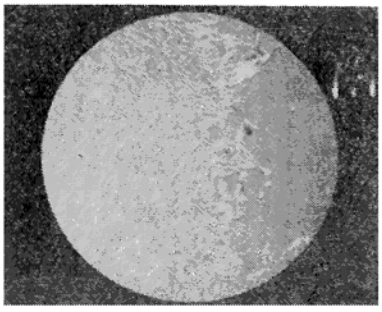

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Fig. 13. Transformation of crystals of *n*-dotriacontane caused by the addition of picric acid (micro-crystallized).

Though the dyes in general gave no remarkable effects, only in the case of "Nippon green B conc." formed micro-crystallization in some parts as shown in Fig. 15.

The examples of almost no effects were the results of photomicrographs of the addition of chloronaphthalene or barium stearate to *n*-dotriacontane, which are shown in Figs. 16 and 17, respectively.

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Fig. 14. Transformation of crystals of *n*-dotriacontane caused by the addition of Santopour (micro-crystallized).

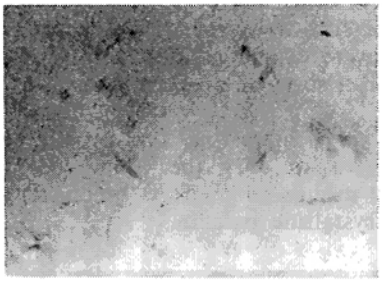

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Fig. 15. Transformation of crystals of *n*-dotriacontane caused by the addition of "Nippon green B conc." (hardly micro-crystallized).

In the case of the asphalt component obtained by propane deasphalting method, its effect was not so remarkable though a little transformation of the crystals of *n*-dotriacontane was seen (Fig. 18).

As mentioned above, two cases were considered; one was of crystalline paraffin, a mixture of various hydrocarbons, in which the

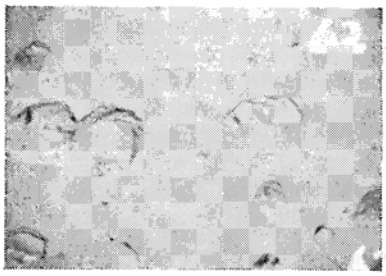
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Fig. 16. Transformation of crystals of *n*-dotriacontane caused by the addition of chloronaphthalene (almost no change).

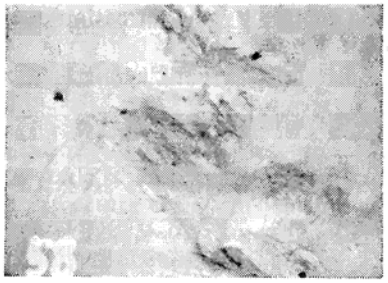
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Fig. 17. Transformation of crystals of *n*-dotriacontane caused by the addition of barium stearate (almost no change).

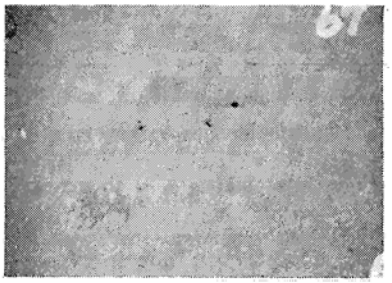
×225

Fig. 18. Transformation of crystals of *n*-dotriacontane caused by the addition of asphalt component (hardly micro-crystallizad).

content of straight paraffins was nearly 90% and containing paraffin side chains, naphthene rings, and aromatic rings; and other was of *n*-dotriacontane, *n*-paraffin series hydrocarbon of carbon number 32. Then, the effects of addition of various organic compounds were different between both, and the composition of the paraffin gave effects on the facility of micro-crystallization of the paraffin. It had already been found[3] that the content of the adductible compounds of the straight chain in the microparaffin was nearly 60%. Accordingly, the easiness of micro-crystallization of microparaffin should be considered to be caused by the existence of more side chains of paraffin in microparaffin than in the crystalline paraffin wax. By observation with the microscope, the phenomenon of micro-crystallization is seemd to be that very fine crystals of plate are rolled up to make minute crystals of needle.

It was found that Santopour, picric acid, *p*-hydroxydiphenyl, and a few direct dyes formed a considerable micro-crystallization of pure hydrocarbons of a straight chain too. It is interesting that all these compounds contain hydroxyl groups and being in somewhat similar structures. Essential investigation will be made by X-ray diffraction, infrared spectrum, observation by electron microscope etc. with regard to the reason why these substances form micro-crystallization of the crystals of paraffin. It should be caused by the fact that the properties of paraffin molecules arranging regularly and growing up to the fundamental crystal of plate are inhibited or obstructed. However, it will be cleared in detail by future studies.

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