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POSSIBILITIES OF MICROCRYSTALLINE WAX PRODUCTION FROM HEAVY VACUUM GAS-OIL FRACTION

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ABSTRACT

In this research an attempt was made to separate wax from Heavy Vacuum Gas-oil which was obtained from the Middle Anatolia Refinery by extraction with different solvents at various temperatures. Methyl isobutyl ketone, water saturated methyl isobutyl ketone (1.9 % by weight), methyl ethyl ketone, acetone, hexane, toluene + methyl isobutyl ketone (2+1 by weight) were chosen as solvents.

Wax solubility in the solvents mentioned has been examined at four different temperatures. Melting point of each wax sample were determined and an attempt was made to characterize hydrocarbon distribution and crystalline structure by gas chromatography and microscopy, respectively.

The best conditions for obtaining microcrystalline waxes from petroleum fractions were determined.

INTRODUCTION

Wax generally refers to a substance that is a plastic solid at ambient temperatures and a low viscous liquid at high temperatures. It deforms under pressure without the application of heat. Waxes which are especially a mixture of straight chain paraffins, have a complex structure. All waxlike materials found naturally are generally called wax, as well as synthetic wax and natural wax. Their uses are usually based on their physical characteristics. These characteristics are resistance to water and water vapour, ductulity, hardness, tensile strength, refractive index, ability to emulsify, molecular weight, melting range and solvent retention (Kirk and Othmer, 1956). Alkanes, wax- and fatty-acids, long chained ketones, and wax- and faty- alcohols are chemically waxes. They are produced from plants, animals and natural sources like petroleum. In petroleum refining, waxes are separated from paraffin distillates, motor-oil wax, residual microcrystalline wax and tank-bottom wax (Kirk and Othmer, 1971; Nelson, 1958).

Many uses of these waxes are given in the following list: Candles, artificial fruits and flowers, polishes, dental waxes, rain clothing, de-icing compound, dehydrated food packages, ship launching grease, blasting supplies, binding agents, stop-off for glass etching, ointments, rust preventation, barrel lining, lining for acid pipelines, beer can lining, metal drum lining, electrical insulations, egg preservatives, capsules, carbon papers, rubber compositions, printing, printing ink ingredient, shoe and leather treatment, sound records, cosmetic creams, lipstics, false eyelashes, adhesive for laminating, laminants for paper, paper board cartons and drums, paper milk bottles, drinking cups, bottle cap liner coatings, cheese and meat coatings, sealing and heat sealing compounds (Bennett, 1975; Warth, 1947).

EXPERIMENTAL

Experimental studies were made with Heavy Vacuum Gas-Oil (HVGO) which is obtained from praffin distillates of the Middle Anatolia Refinery, Kırıkkale, Turkey.

In this study, waxes were separated from HVGO by extraction and precipitated by cooling (Demirel, 1988). Methyl isobutyl ketone (MIBK), water-saturated MIBK (1.9 % by weight), methyl ethyl ketone (MEK), acetone, hexane, toluene + MIBK (2+1 by weight) were used as solvents, and experiments were made at various temperatures, 30°C, 0°C, —10°C and —20°C. After waxes were obtained, each wax sample was examined and composition was determined.

HVGO was mixed with solvents to a feed ratio of 3:1 (wt-wt) and the slurry was heated to 30°C on a heating bath for 3–4 hours. Thus the soft wax components and the oil were formed liquid phase and hard wax components were formed solid phase. The slurry was then centrifuged at 30°C in order to separate solid and liquid phases. The waxy mass was filtered by an insulated funnel at the same temperature. Before the solvents were removed, the wax cake was washed with the same solvents to a feed ratio of 1:1 (wt-wt) at the same temperature.

In addition to the separation of wax at 30°C, it was also separated at 0°C, —10°C and —20°C. HVGO was mixed with these solvents to a feed ratio of 3:1 (wt-wt) and the slurry was heated to 35–40°C and kept until the clear solution was obtained. These solutions were slowly cooled to 0°C, —10°C and —20°C, and precipitation was observed as clouding by cooling. These solutions were filtrated by isolated funnels at the temperatures mentioned (Agrawal and Anand, 1975; Agrawal and

Chobey, 1978; Agrawal and Gupta, 1981; Agrawal and Joshi, 1984; Anand et. al., 1970; Anisimov and Mitrofenov, 1970; Freund et. al., 1967; Johannes et. al., 1967; Kumar et. al., 1972; Skarpa, 1978).

The yield and melting points (ASIM D–127) were found; hydrocarbon distributions were determined by gas chromatography (Packard, 427) (Figure 1–3); molecular weight was found by molecular weight apparatus (Hitachi-Perkin Elmer Model 115). The wax samples were then photographed by Leitz Orthomat-W Micrography apparatus to establish their crystal structures.

RESULTS AND DISCUSSION

When the molecular weight of waxes which were obtained at various temperatures was examined, it was found that the molecular weight increases with an increase of the extraction temperature as given in Figure 4. These studies show that extraction at ambient or higher than ambient temperature is more suitable to obtain higher molecular weight waxes. On the other hand, as shown in Table 1, the relation between melting point and molecular weight is approximately the same except for a deviation of result in wax which was separated by acetone.

In Figure 5, it is shown that an increase of extraction temperature causes a decrease in the wax yield. Maximum yield is obtained with acetone and MEK, respectively. Although the wax yield considerably changes when asetone is used, MEK doesn't effect it except at low temperature. Other solvents cause approximately the same effect to yield. Wax yields by MEK and hexane are quite constant at 0°C and over 0°C, but MIBK and saturated MIBK give different results in the same conditions.

Solvents which have ketone structure have no affinity for waxes and they never dissolve hydrocarbones. On the contarary, they crystallize waxes and thus separate from oils. Ketone structure solvents, especially MIBK, naturally produce waxes which have much higher melting points. Although acetone has a ketone structure, it doesn't give the same results with MIBK as a result of being a very polar solvent for hydrocarbons. Solvents like toluene and hexane solvate oils efficiently and they remove oils from HVGO fraction, but don't crystallize waxes which have higher molecular weight. Chromatograms of waxes which are obtained at 30°C were given in Figure 1–3. It was observed that chromatograms from this study and other literature provide correlations about paraffin contents (Chen and Lucky, 1970;

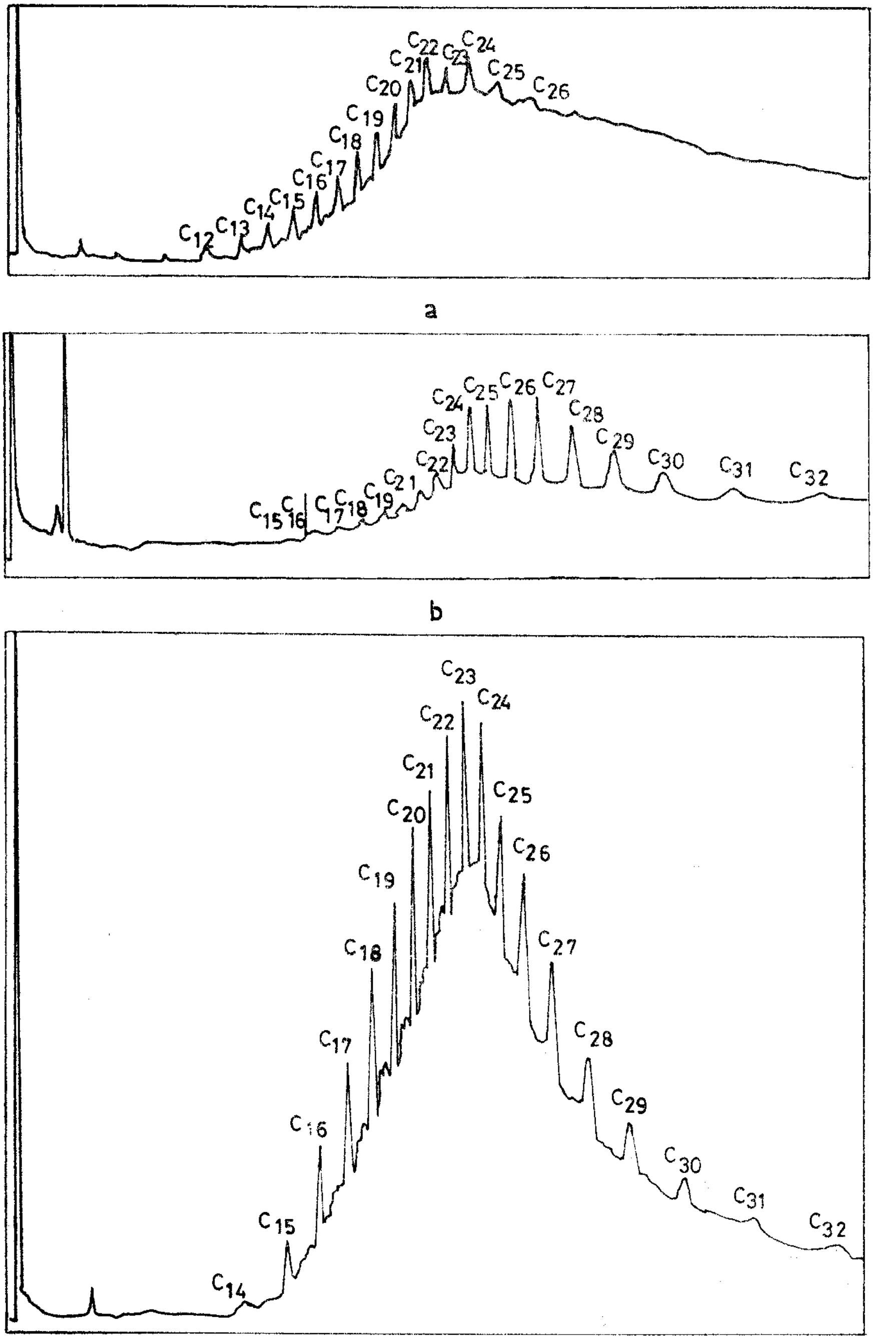

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Figure 1. a) Gas chromatogram of HVGD, gas chromatograms of wax samples which are separated by b) MIBK, c) Water-saturated MIBK at 30°C.

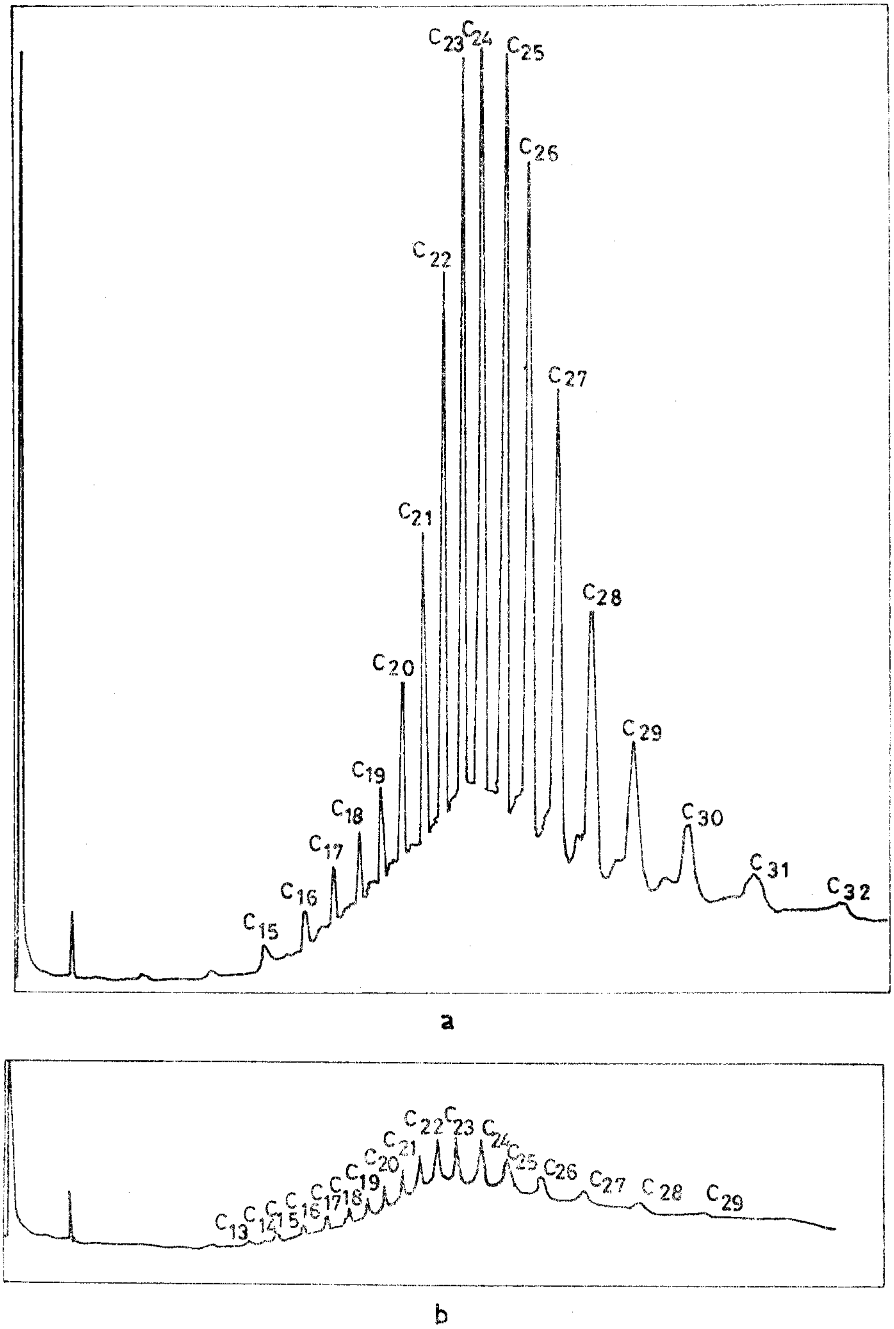

Figure 2. Gas chromatograms of wax samples which are separated by a) hexane, b) MEK at 30°C

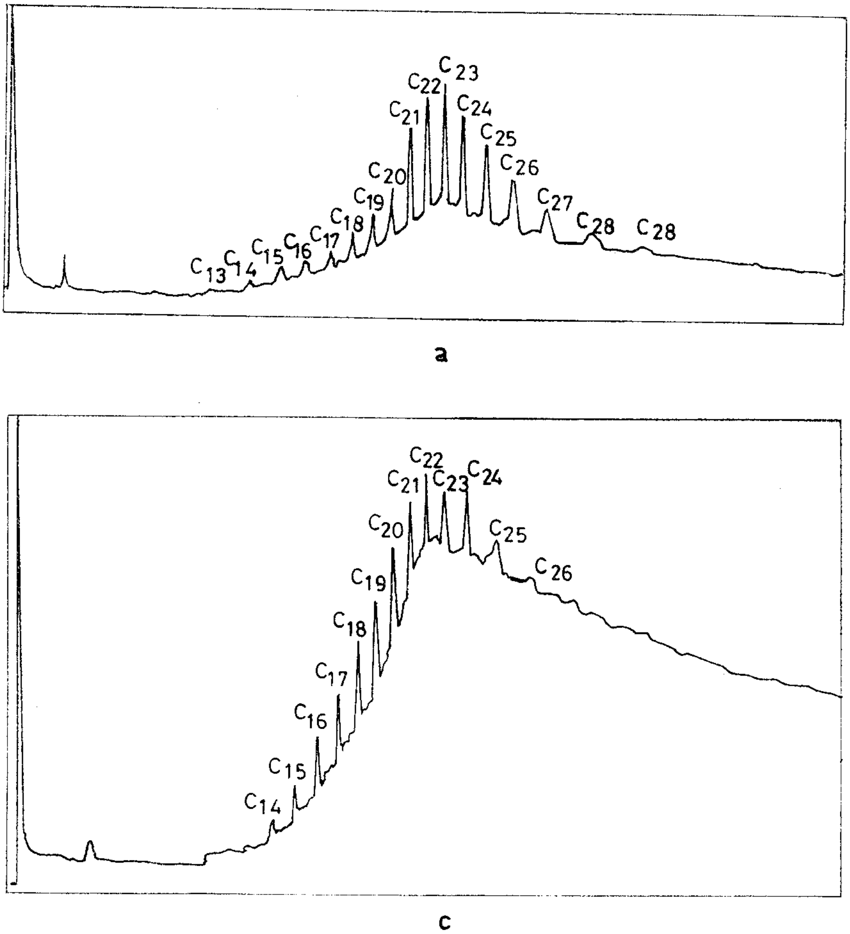

Figure 3. Gas chromatograms of wax samples which are separated by a) Toluene+MIBK, b) Acetone at 30°C.

Lawrance et. al., 1982; Demirel, 1988). It is also evident from Table 1 and Figures 4 and 5 that the melting points and molecular weights also correlate.

To determine the crystal structure of waxes, wax samples were photographed under microscope as can be seen in Figures 6–9. Waxes which were obtained with MIBK and water saturated MIBK at 30°C crystallize in needles, but then change to a honeycomb structure at lower temperatures (Demirel, 1988). Waxes separated with MEK and MIBK have different crystals (Figure 6–7) (Demirel, 1988). Wax crystals se-

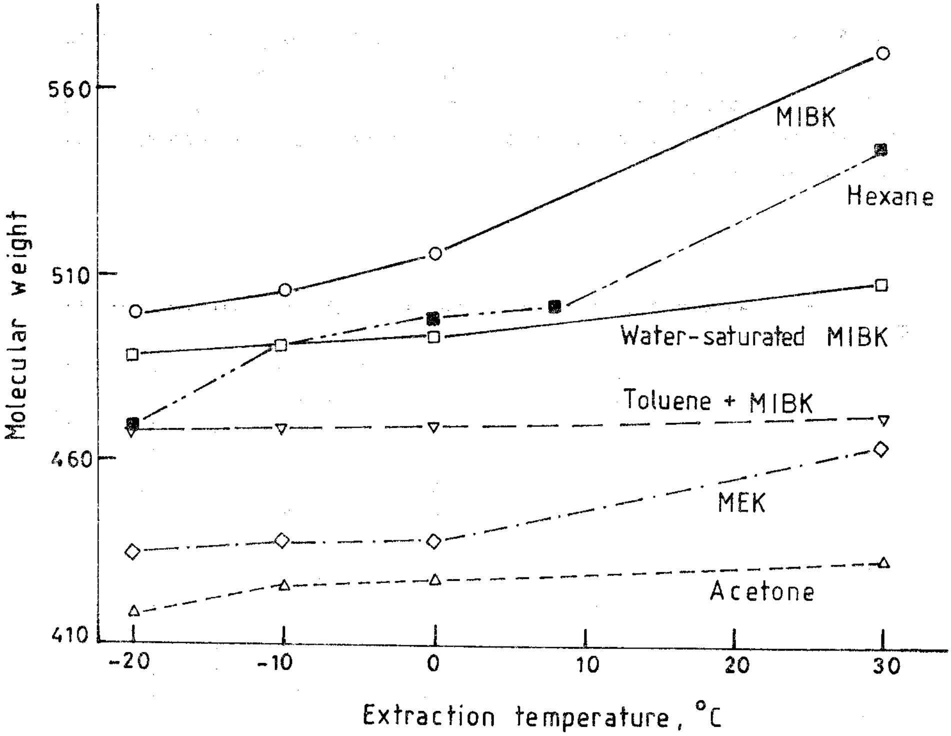

Figure 4. Variation of molecular weight with extraction temperature.

parated with acetone are considerably different from those separated with other solvents (Figure 8) and wax crystallizes into sphere-like particles or flat plates. It can be stated that these are unqualified paraffin structures (Warth, 1947). As observed from the melting point, molecular weight and gas chromatography studies, acetone cannot completely separate oils from HVGO fractions. If Figure 9 is examined, the importance of extraction temperature can be understood. While wax crystallizes in needles at 30°C, it crystallizes as plate structure at lower temperatures (Demirel, 1988).

CONCLUSION

MEK, water saturated MIBK, hexane and MIBK are found to be effective for the separation of higher molecular weight and melting point waxes from HVGO fraction. Crystal structure of waxes which were obtained at low tempeatures are almost paraffinic and change to microcrystalline structures at higher temperatures. The possibility of microcrystalline wax production from HVGO has been proven and it can be stated that although microcrystalline structure may be obtained at higher temperatures than 30°C, HVGO is not a very suitable source to produce microcrystalline waxes at high temperature because of a decrease in the wax yield.

Teble 1: Yields, melting point and molecular weight of waxes separated from HVGO at various temperatures.

Solvent	Extraction Temp. (°C)	Yield (%)	Melting Point (°C)	Mole. Weight
MIBK	30	0.23	77	573
	0	3.84	63	517
	-10	4.80	60	506
	-20	8.408	58	500
	30	2.81	72	510
Water saturated MIBK (1.9 % by weight)	0	3.51	63–64	495
	-10	4.11	60–61	492
	-20	5.91	57–58	489
MEK	30	9.39	50–51	466
	0	9.54	50	439
	-10	9.60	49	438
	-20	13.16	48	435
Acetone	30	57.83	34	434
	0	62.05	34	428
	-10	64.04	34	426
	-20	65.67	34	418
Toluene + MIBK (2+1 by weight)	30	1.32	60	474
	0	2.40	50	470
	-10	3.72	48	469
	-20	9.00	47	468
Hexane	30	0.39	68	547
	0	0.41	57	500
	-10	4.32	45	492
	-20	11.68	41	470

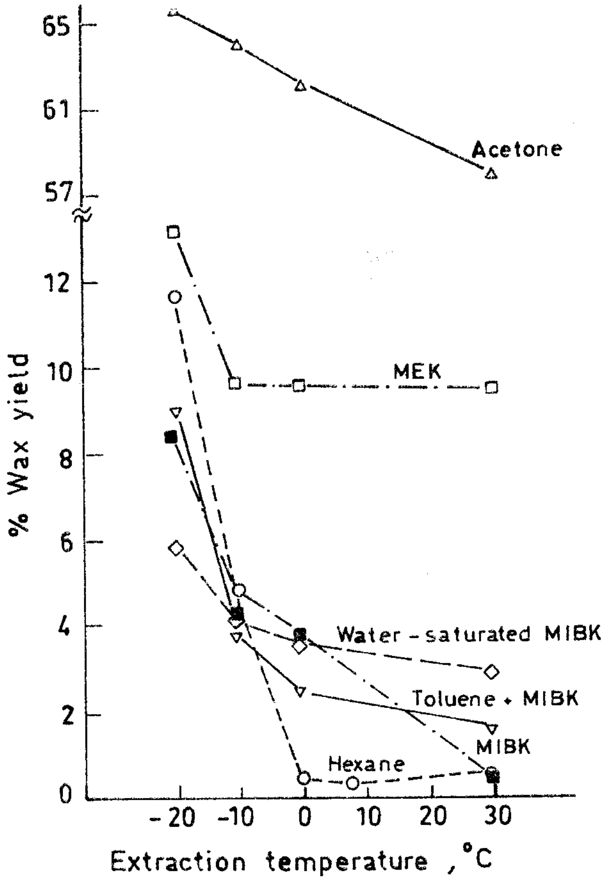

Figure 5. Variation of wax yield with extraction temperature.

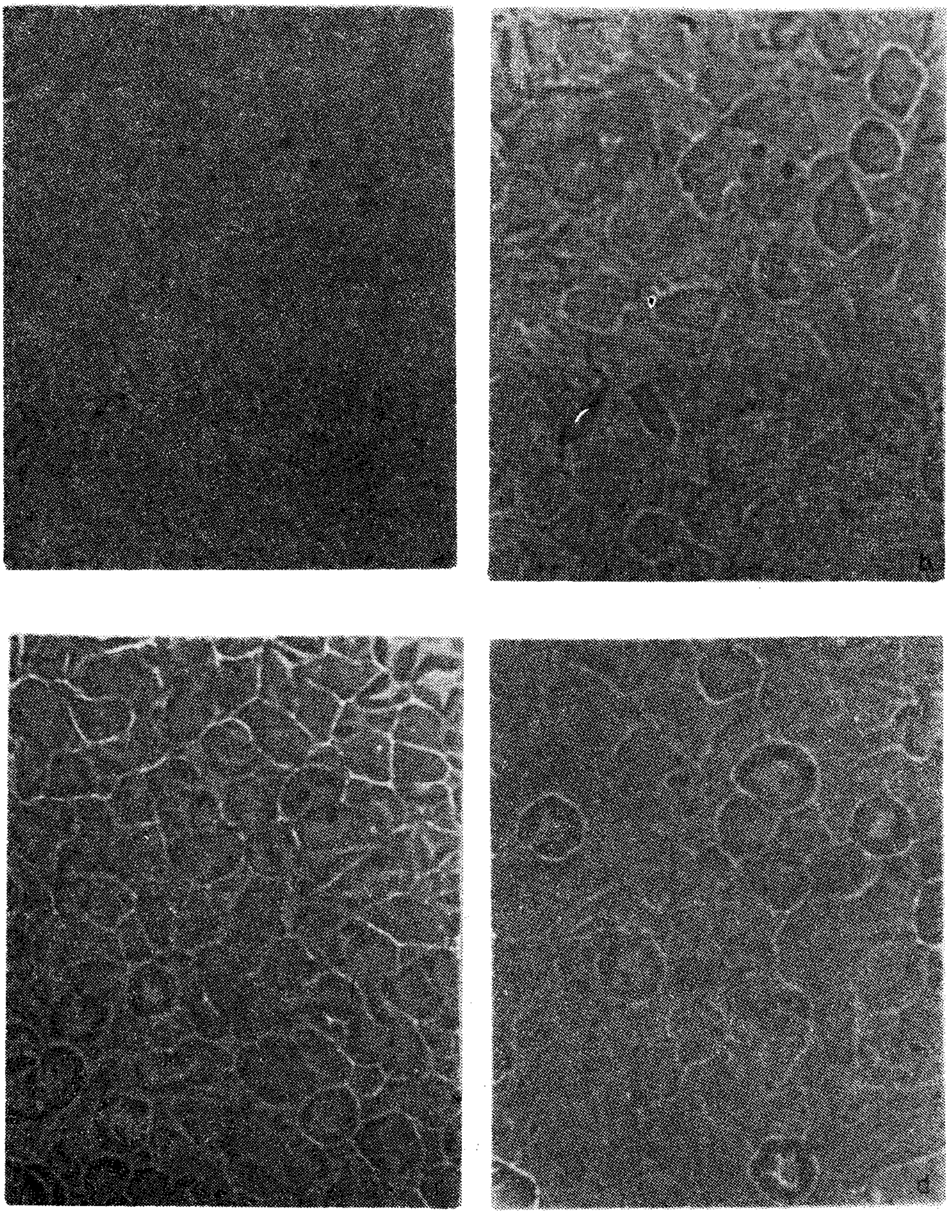

Figure 6. Photographs of wax crystals which were separated by MIBK at a) 30°C, b) 0°C, c) –10°C and d) –20°C (x200).

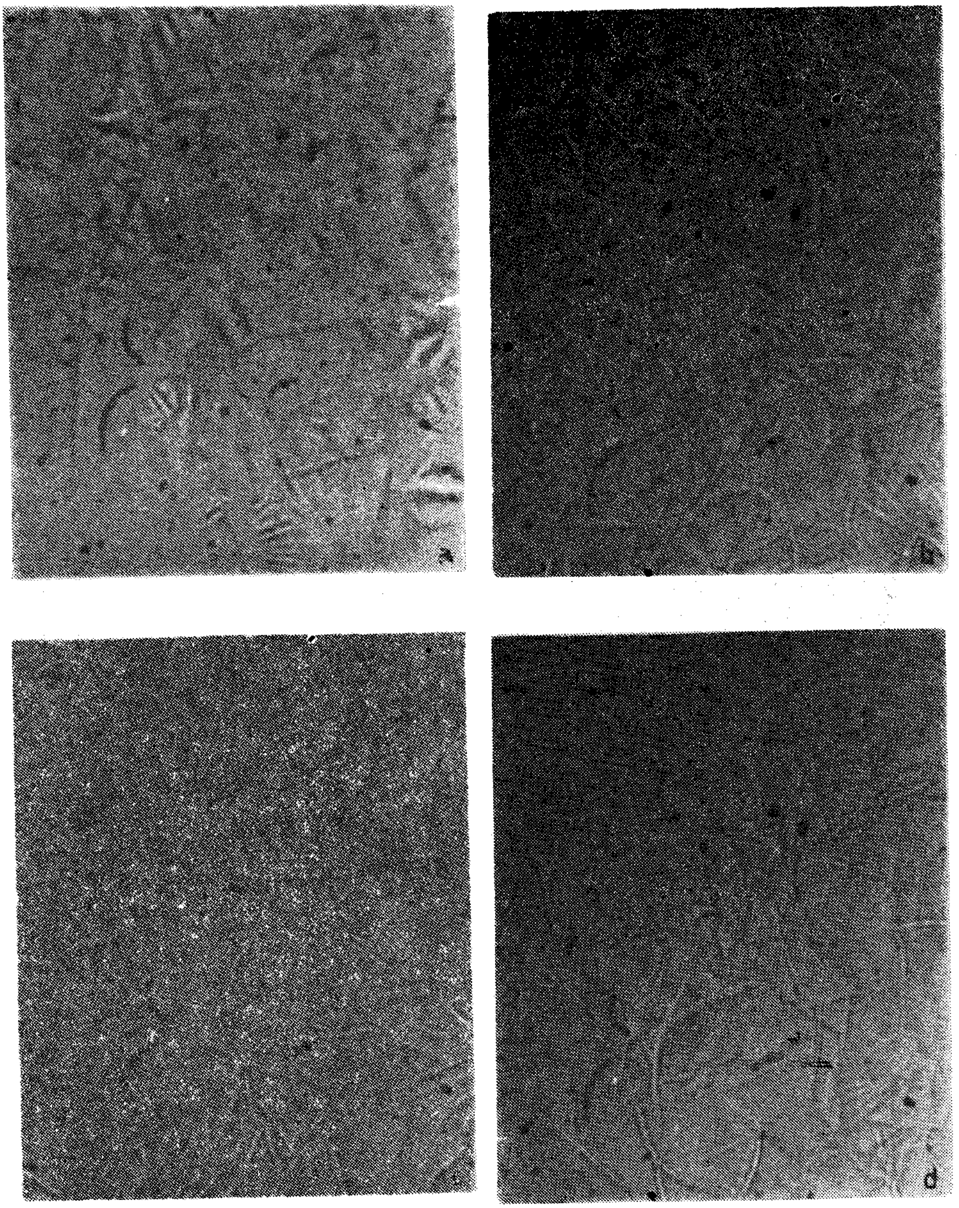

Figure 7. Photographs of wax crystals which were separated by MEK at a) 30°C, b) 0°C, c) -10°C and d) -20°C (x200).

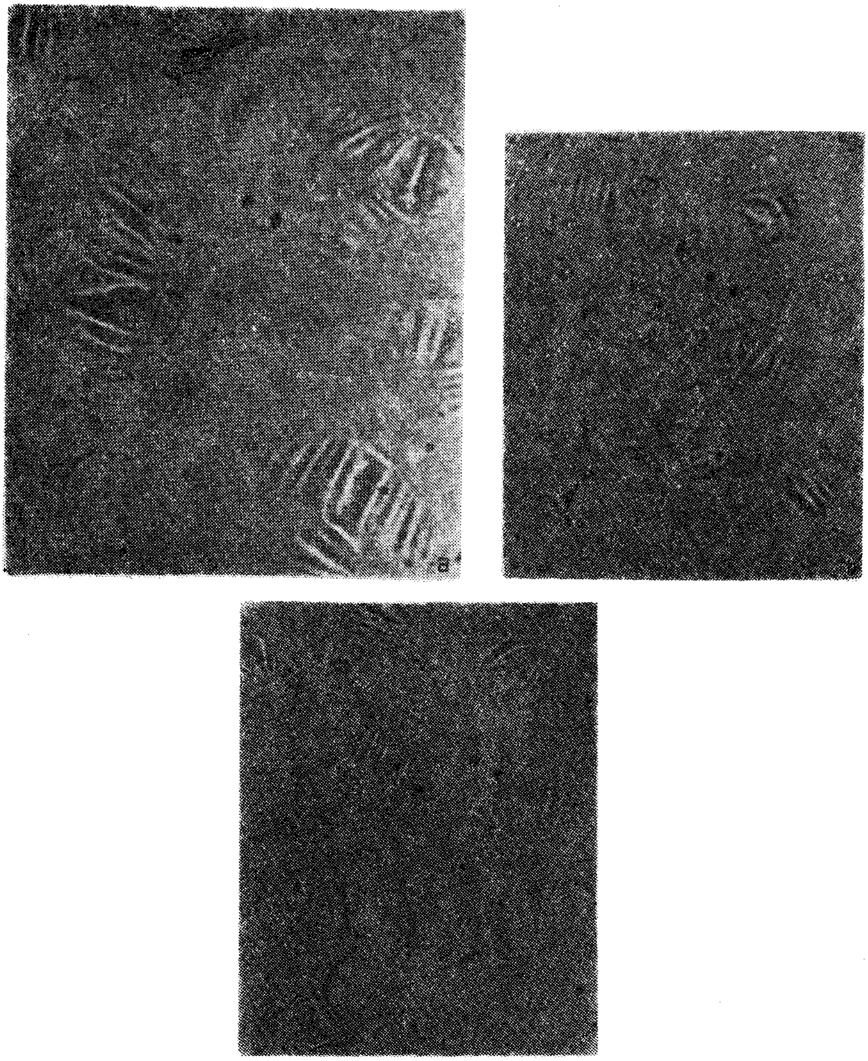

Figure 8. Photographs of wax crystals which were separated by acetone at a) 0°C, b) –10°C and c) –20°C (x200).

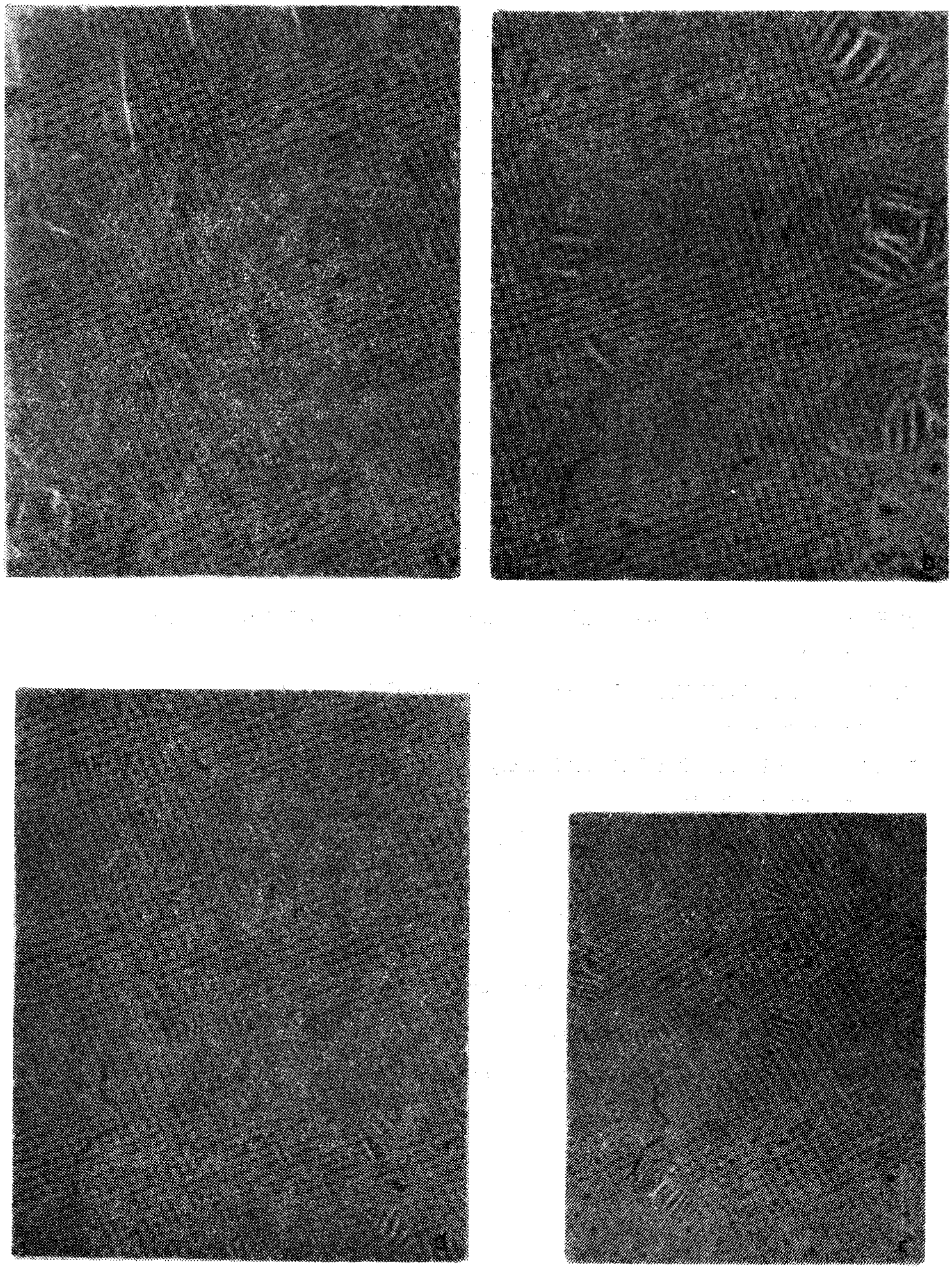

Figure 9. Photographs of wax crystals which were separated by Toluene+MIBK at a) 30°C, b) 0°C, c) -10°C and d) -20°C (x2000).

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