

The data of Table III seem to indicate that the ethyl linoleate was acting like a chain transfer agent since the higher the proportion of it in the monomer mixture, the lower the intrinsic viscosity of the polymer formed. This general trend is shown by Run IX even though the 45% mixture is out of order.

Although the ester appears to limit chain length, its action is not solely that of a chain transfer agent. Table IV shows that there are many more ester groups per molecule than to be expected if the linoleate ester functioned as a modifier of the mercaptan type studied by Snyder *et al.* (15) and by Wall and co-workers (16). These investigators found an average of one modifier group per chain. It is probable that the ester both copolymerizes with the styrene in the normal way and also exerts some modifying action, as suggested by Hewitt and Armitage (5). The tendency to copolymerization is most marked in the case of the bulk polymerization (VII) since the product in this case had a high ester content without a correspondingly low molecular weight.

Summary

The emulsion polymerization at 40°C. of mixtures of oxidized ethyl linoleate and styrene with potassium persulfate as catalyst yielded copolymers containing a maximum of one mole of ester per thirteen moles of styrene. A product of similar composition was obtained by bulk polymerization at 80°C.

When the amount of ester in the monomer mixture was increased to 50 per cent in the emulsion polymerization, the ester content of the polymer was

increased and the molecular weight and yield were decreased.

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Studies on Candelilla Wax. II. Its *n*-Paraffins

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THE traditional methods of isolating wax paraffins, described by Chibnall *et al.* (1) and Leys (5), are laborious and time-consuming. Both methods require an initial saponification of the wax, which often is very difficult. Moreover, the resulting paraffin fractions are impure and require further purification. For the purpose of isolating the hydrocarbons of candelilla wax required for this investigation, there was developed a simple, rapid chromatographic procedure which eliminates involved treatment of the saponified wax. The method described is suitable for large-scale work and reduces the time required for the isolation of the paraffins to a matter of a few hours.

Isolation Procedure. A column, 14 inches long and two inches in diameter, was packed with activated alumina (Grade F-20, Aluminum Ore Co.). The candelilla wax was dissolved in dry petroleum ether, heating being necessary to dissolve the wax. The cooled wax solution was then drawn rapidly through the column by gentle suction, a yellow band making itself evident. On cooling, the wax solution gelatinized somewhat; this however presented no particular difficulty. After the washing of the column with petroleum ether, the solvent was evaporated from

the colorless percolate. A white residue of paraffins was obtained. These, redissolved in petroleum ether, were passed through a fresh column of alumina, after which the recovered paraffins were heated with concentrated sulfuric acid. The fact that very little blackening of the paraffins occurred when isolated by this procedure attested to their purity. After removal of the sulfuric acid by washing with water the dried paraffins were crystallized from petroleum ether whereupon beautiful white crystals were obtained.

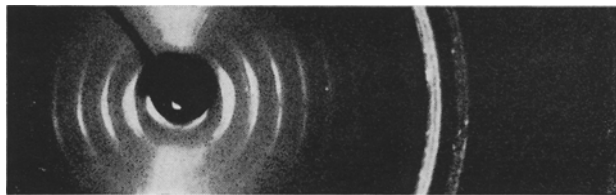
The same procedure was used for the quantitative determination of paraffins in this wax. Approximately 50-gram samples were used, the wax solution being passed through only one column of alumina. The paraffins were heated with sulfuric acid although this treatment may be omitted if candelilla samples are to be analyzed as a routine operation. After filtration and washing, the paraffins were brought to constant weight. Excellent checks were obtained; the hydrocarbon content averaged 52.2%.

Separation of Hydrocarbon Fractions. Numerous workers (6, 8) have used adsorption techniques to separate paraffin mixtures. In 1947 Hirschler and Amon (4) found that even geometric isomers of

the paraffins could be separated by adsorption on silica gel. Adsorption therefore seemed to us to offer greater possibilities than lengthy fractional crystallization procedures as a tool for the partial separations of candelilla paraffins.

Accordingly a glass tube 0.5 inch in diameter and 65 inches long and constricted at one end, was filled with silica gel (Davison, 28- to 200-mesh range). Before use all silica gel was heated overnight in a muffle furnace. Charges of paraffins dissolved in benzene were then passed through the column. The benzene had been first dried over calcium chloride and then purified by passing one liter through a 200-gram column of silica gel. This removed a large amount of adsorbable impurities manifested by the formation of a yellow zone on the silica gel column.

After many days, when the percolate began to drip from the bottom of the tube, fractions were arbitrarily collected, their paraffins recovered, and those with the widest spread in solidification points were passed through a fresh column of alumina. X-ray analyses were made of the best fractions. All photographs—see Figure 1 for typical case—were taken with the



Total hydrocarbon mixture
42.03 Å

FIG. 1. Powder photograph of hydrocarbon mixture.

General Electric XRD unit, using iron radiation with a manganese dioxide filter. Two-hour exposures were made. The paraffin fractions intended for the X-ray analyses were crystallized from benzene. It was necessary that crystallization proceed from dilute solution and that the benzene evaporate spontaneously at room temperature, otherwise poor photographs were obtained.

The long spacings together with other physical data are recorded in Table I. The data for Fraction I agree fairly well with the synthetic mixture (80% C_{31} + 20% C_{29}); the long spacing 41.4 being somewhat smaller, indicating that the percentage of C_{29} is perhaps a little higher. The data for Fraction II are consistent with that pertinent to Chibnall's (2) (95% C_{31} + 5% C_{33}) although its long spacing and solidification points are higher, indicating that C_{33} is present in greater quantity in our natural mixture.

TABLE I
Physical Data on Hydrocarbon Mixtures

Sample	Long spacing	Solidification point	Melting point	First transition point on heating
		Å	°C.	°C.
Total hydrocarbons	42.03	67.5	67.8-68.0	61.2-61.4
C_{29} (5%) + (C_{31} 90%) + C_{33} (5%) ¹	42.0	67.8	61.0
Fraction I	41.4	66.1	66.4-66.5	59.7-59.9
C_{29} (20%) + C_{31} (80%) ²	41.5	66.0	66.6-66.8	60.0-60.5
Fraction II	42.20	67.7	68.1-68.3	61.2-61.5
C_{33} (5%) + C_{31} (95%) ¹	42.0	67.4	67.9-68.0	62.0-62.2
Fraction III	41.71	67.4	67.6-67.9	60.6-60.9

¹ Chibnall *et al.*, see Ref. 2.

² Piper *et al.*, see Ref. 7.

The data of Fraction III indicate that a smaller percentage of C_{33} is present than in the synthetic mixture. Finally the total paraffin fraction is obviously composed of the C_{29} , C_{31} , and C_{33} hydrocarbons, the data of our mixture agreeing with that of the ternary synthetic mixture. Fraps and Rather (3) in an early paper reported the C_{31} hydrocarbon. Later, Chibnall and co-workers (2) reported the C_{31} and C_{33} paraffins.

Attempts at Ketone Isolation. All efforts to establish the presence of ketones ended in failure. The unsaponifiable matter, recovered from an alkaline hydrolysis in ethylene glycol medium, was heated with hydroxylamine hydrochloride in the presence of pyridine. Attempts to isolate oximes by adsorption on activated alumina proved fruitless. Experiments aimed at isolating colored ketone derivatives of 2,4-dinitrophenylhydrazine by adsorption likewise were unsuccessful.

Summary

A simple, rapid adsorption method for the isolation of candelilla paraffins has been described. Use of the method as a quantitative procedure yielded 52.2% paraffins.

X-ray analysis and other physical data indicated that the principal candelilla paraffin was the C_{31} compound. The C_{29} and C_{33} homologues were also found to be present, C_{29} being reported for the first time.

The presence of ketones could not be established.

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