STUDIES IN THE PROCESSING AND UTILIZATION OF GREASE-LIKE WASTE PRODUCT FROM THE EPHEDRINE PLANT OF MARKER ALKALOIDS, QUETTA

G. Mustafa Ali and Riaz Ahmad

Paints and Plastics Research Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

(Received June 16, 1966; revised June 15, 1968)

A grease-like tacky product of greenish black colour is obtained as a by-product in considerable quantities (1500--2000 lb per month) at the Ephedrine Processing Plant of Marker Alkaloids, Quetta. The greasy nature and high acetyl number led to the processing of this material with a view to get products of industrial utilization in wax-based compositions. Methods of processing and the characteristics of the resulting products have been described in detail. Possible uses of such products have also been suggested in this paper.

Introduction

A grease-like tacky product of greenish black colour is obtained as a by-product in considerable quantities (1500-2000 lb per month) at the Ephedrine Processing Plant of Marker Alkaloids, Quetta. The physical and chemical constants of the raw grease are as follows: Moisture 8%; inorganic matter (dust) 2%; acid number 20–21; saponification number, 135–140; iodine number 100–104; unsaponifiable matter 40–45%; acetyl number 77–80; and m.p. 40°–45°C.

Previous work reported by Siddiqui and Hahn[1] was limited to the extraction and characterisation of saponifiable and unsaponiable matter of the grease. The present investigations were undertaken to study the possible industrial utilisation of the grease employing the methods of recrystallisation, sulfonation, decolourisation with subsequent recrystallisation, distillation with or without vacuum, and deodourisation.

Processes

Recrystallisation.—When the grease was recrystallised thrice with hot alcohol, a resin-free, a pale green colour solid was obtained in a yield of 20%. The product melted at 63–65°C. The recrystallisation reduces iodine number, unsaponifiable content and the acidity but improves colour and hardness of the product. Acid value 13.8; saponification value 131–133; iodine value 56–58; unsaponifiable content 25–30%.

Sulphonation.—The unsaponifiable fraction of the grease is known to contain nearly 12% alcoholic substance, named Ephedra Alcohol.[1] Sulphonation of grease and of the unsaponifiable matter was undertaken but the resultant products did not show any significant detergent properties.

Decolourisation.—The raw grease was decolourised by using bleaching materials like fuller's earth and activated charcoal. Varying percentages of decolourising substances were used. 10% solutions of grease in mineral turpentine were found suitable to avoid great losses in the process of bleaching. Even with 200% decolourising material the greenish black colour of the original grease changed to dark brown. With repeated recrystallisations (usually three) with hot alcohol or acetone this dark brown product yielded almost a colourless solid substance but the yield was low (10% on the weight of the raw grease). No change was observed in the characteristics of the refined product when compared with the recrystallised material.

Distillation under Vacuum.—When subjected to a temperature of 300–350°C under a reduced pressure of 5–10 mm Hg, it yielded a butter-like brown product m.p. 40–45°C. Nearly 75% of the grease could be distilled under these conditions. Fractional distillation under high vacuum at different temperatures gave soft waxy products with an objectionale odour. Recrystallisation (twice) of these products with hot alcohol or acetone yielded fairly white substances. The physical and chemical constants of these fractions have been listed in Table 1.

Further quantities of waxy products were obtained from the respective mother liquors. Insoluble residues obtained during hot alcoholic recrystallisation of these distillation products were resinous and had low acid and saponification numbers.

Distillation without Vacuum.—Distillation of the grease at high temperatures (300° and above) without vacuum gave dark brown-coloured oderiferrous oily liquids (Table 2)

Odour in raw grease caused by the presence of essential oils was removed by steam distillation. The essential oils thus obtained were employed as perfumes in toilet soap formulations. The typical smell of these products was not found pleasant and durable.

Results and Discussion

Recrystallisation of raw grease with hot alcohol reduces iodine number, unsaponifiable content and the acidity. The lowering of iodine number, acidity and unsaponifiable content in the process of recrystallisation of raw grease with hot alcohol shows the partial removal of unsaturated material, free fatty acids and the compounds present in the nonsaponifiable portion, namely alcohol and hydrocarbon, whose occurance has been reported by previous researchers. The improvement in hardness of the recrystallised product (melting point rose from 45–50°C to 63–65°) is a further indication of the loss of unsaturated substances. The reducation in colour in the process of recrystallisation indicates the removal of the chloroplast pigments (chlorophyll, xanthophyll and carotene) whose presence in a considerable quantity has been mentioned by Siddiqui and Hahn.[1] Attempts are being made to isolate the green pigment (chlorophyll) from the alcoholic extracts of raw grease.

The waxy nature of the recrystallised grease could possibly be exploited for its use in wax-based polishes and cream composition. Decolourisation of grease by physical methods does not appear to be suitable as large amounts of fuller's earth and activated charcoal are required. Chemical bleaching could possibly be employed to overcome great losses of material during this operation.

Distillation under vacuum and without vacuum provides a good means to obtain products of interesting characteristics after recrystallisation with hot alcohol (Tables 1 and 2). Among the three fractions the first one collected in the process of distillation under vacuum appears to be quite useful having properties close to those of bees-wax and could probably be utilized as its substitute in polish compositions. Moreover, high acetyl value (64) of this material makes it very suitable to impart some properties of hard waxes like carnauba. The other two fractions collected in the above process do appear to have properties of waxy materials (Table 1) but their higher values for saponification and unsaturation make them inferior in grade and moreover their yield is comparatively low.

Further yield of these substances extracted from the respective mother liquors was discarded due to their dark brown colour and high free fatty acid content. The insoluble residues resulting from the hot alcoholic recrystallisation of the above mentioned three fractions do not seem to have much fatty matter as indicated by their low acid and saponification numbers.

The fractions collected in the process of high temperature distillation of grease without vacuum show a remarkable decrease in the saponification and iodine numbers and an increase in the yield. This could possibly be attributed to the distillation of unsaturated fatty matter from grease in the early stages of the process leaving behind more unsaponifiable portions. Low values for the acetylation of these fractions obtained through distillation do not justify their use in waxy compositions.

Table 1

Fraction No.	Temp.	Yield %	M. p.	A.V.	S.V.	I.V.	Acet. V.	Unsap. %
1	300–310°	5.3	62–70°	49.7	30–32	11–13	64.0	60–63
2	310–325°	3.3	56–57°	38.4	53–55	44–45	—	—
3	325–345°	2.6	58–60°	58.2	50–52	28–29	—	—

Table 2

Fraction No.	Temperature	Yield %	A.V.	S.V.	I.V.
1	300–310°	3.5	38.5	80–83	139–140
2	310–315°	9.5	82.4	79–82	124–125
3	315–330°	4.75	73.5	83–84	90–92
4	330–345°	13.25	57.1	61–63	95–97
5	345–375°	22.0	6.8	25–27	74–75

The first fraction with a high percentage of unsaturated fatty matter could be further investigated to find its usefulness. The lower amounts of fatty substances as shown by its number for saponification discard the possibility of its use in paint and varnish industry alongwith other unsaturated fatty oils.

Conclusion

The results indicated in the paper show no immediate utilization of the waste product. However, trials carried out for the utilization of raw grease in the emulsion form for the waterproofing of hard board and chip board showed positive results. This material, however, can only be employed for such purposes where colour is no consideration.

Acknowledgement.—The authors wish to express their thanks to the Management of Marker Alkaloids, Quetta, for the supply of the raw material for the present investigations and to Mr. M. Aslam of the West Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Lahore for helpful suggestions and discussions.

Reference

1. N. Siddiqui and G. Hahn, Pakistan J. Sci. Ind. Res., **2**, 245 (1959).