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MANUFACTURE OF DARK FACTICE FROM RUBBER SEED OIL

BY

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INTRODUCTION

Factice has been known in the rubber industry from a very long time; it is a rubber substitute, which is essential to be added to rubber, in preparing compounds of different composition for the manufacture of certain rubber articles, like erasers, tubes and tyres. All rubber technologists are familiar with the appearance of factice, which is not merely something occasionally mixed into rubber but is a compounding ingredient of unique properties for which, appropriately enough, there is no substitute (Flint, 1955). Factice gives to moulded, calendered, extruded, dipped and proofed goods a smooth finish and supple handle which cannot be obtained by any other compounding ingredient. Mould designs are reproduced with great fidelity. The surface finish of rubber goods is also improved because factice restrains the blooming of sulphur and oils. Factice imparts resistance to surface oxidation and to ozone, and improves resistance to moisture. Factice which is normally classified as " white " and " dark " is the product of vulcanization of an unsaturated oil, with sulphur chloride or sulphur. Though factice is used in industrial enterprises in Ceylon, at the moment there is no organization in the country manufacturing this product.

Recently a joint project was carried out by the Rubber Research Institute of Ceylon and Lever Brothers (Ceylon) Limited on the collection of rubber seeds and extracting oil from them (Nadarajah, 1969). It was found that rubber seed oil is suitable for the manufacture of factice, as it has the necessary amount of unsaturated fatty acid content, vital for factice manufacture. The colour of factice is directly connected with the iodine value of the oil used. The higher the iodine value, the darker is the factice. Good quality factice is formed from oils having an iodine value of 80 — 110. The content of the saturated acids should be below 5%; otherwise the factice will have a soft or tacky texture. The absence of polyolefinic acids other than linoleic acid is also essential (Carrington, 1962).

Application of dark factice

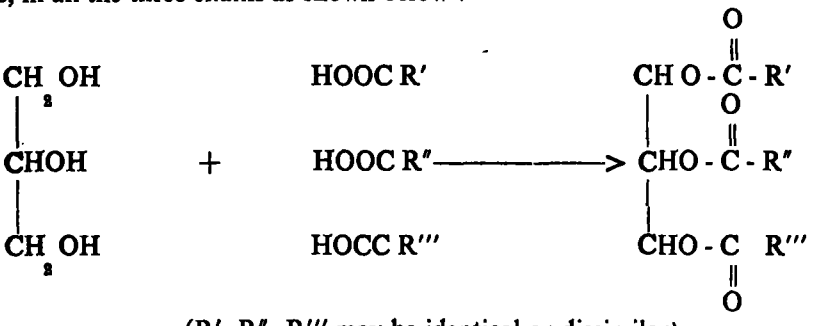
The content of dark factice will vary from 5 to 10 parts per hundred of rubber (pphr) in, say, shoe upper stocks ; 10 — 15 pphr in cable insulation and ebonite ; 15 — 20 pphr in cycle tubes ; 20 — 30 pphr in extruded articles ; 30 — 40 pphr in roller cover stocks ; to 100 pphr in double texture proofed fabrics (Anon, 1956).

During the manufacture of extruded articles the addition of factice to a stock for extrustion gives ' body ' to the uncured compound and reduces the danger of collapse during cure. Factice aids the production of smooth compounds of dimensional stability and reduces swelling of the stock at the extruder die.

Chemistry of factice

The oils used in the manufacture of factice have saturated and unsaturated fatty acids in the form of triglycerides. The greater the content of unsaturated fatty acids the better the factice will be, as the reaction of vulcanization with sulphur or sulphur chloride is a reaction of crosslinking of the double bonds present in the acid chains.

Some of the fatty acids present in the oils are stearic, palmitic, oleic, arachidic, linoleic and linolenic. The triglycerides may be possessing the same or different acids, in all the three chains as shown below :—



(R′, R″, R‴ may be identical or dissimilar)

The fatty acids are also classified as follows :—

Stearic acid $CH_3(CH_2)_{16}COOH$

Palmitic acid $CH_3(CH_2)_{14}COOH$ Saturated acids

Arachidic acid $CH_3(CH_2)_{18}COOH$

Oleic acid $CH_3(CH_2)_7 CH = CH(CH_2)_7 COOH$ Mono-unsaturated acid

Linoleic acid $CH_3(CH_2)_4 CH = CHCH_2CH = CH(CH_2)_7 COOH$ Poly-unsaturated unconjugated

Linolenic acid $CH_3CH_2CH = CHCH_2CH = CHCH_2CH = CH(CH_2)_7 COOH$

The exact way in which sulphur is reacting with triglycerides during factice formation is unknown. There is a large number of proposals for this (Clark, 1962; Flint, 1955).

The mechanism of the reaction of sulphur with oil is the nature of a polar mechanism and not a free radical mechanism (Ross, 1958 ; Bateman *et al.*, 1958).

It is the presence of linoleic or linolenic groupings in the oil which render it reactive towards sulphur.

Some of the oils which are used in the manufacture of factice, are rapseed oil, linseed oil, and castor oil. Comparison of the properties of our rubber seed oil with linseed oil, is as follows :—

COMPONENT FATTY ACIDS % BY WEIGHT (GUNSTONE & HILDITCH, 1946)

	Rubber seed oil (Malaya) Iodine value 134·5	Linseed oil (India) Iodine value 182·0
Palmitic	10·6	9·3
Stearic	11·5	4·7
Arachidic	1·0	1·1
Oleic	17·2	13·1
Linoleic	35·8	17·1
Linolenic	23·9	54·7

Note : Malayan rubber seed oil is very similar to rubber seed oil from Ceylon.

The presence of a high percentage of linolenic acid in linseed oil gives the oil more drying properties, and the presence of less linolenic and more linoleic acid in rubber seed oil confers on the oil a lesser tendency to yellow.

It is believed (Carrington, 1962) that the presence of free fatty acids in oils is a drawback towards factice formation. Linseed oil has a free fatty acid content of about 1·8% by weight while rubber seed oil has much more.

The difficulties which occur during the reaction of rubber seed oil with sulphur are : (1) to control the temperature of the reaction, (2) to have regular heating of the full mass, (3) to minimise the temperature of the reaction, and (4) to minimise the period of the reaction itself and the secondary treatment.

These difficulties were overcome in a small scale, in the work done, as will be mentioned later. There is no necessity for a secondary treatment and the solid mass is formed in a very short period. However, the evolution of toxic fumes is a difficulty which involves the engagement of suitable precautions.

EXPERIMENTAL

Though it is mentioned in the literature that, when an unsaturated oil is heated with sulphur at about 130 — 160°C the temperature of the mixture increases (the reaction between sulphur and oil being exothermic) and the mass is converted into a gel within a few hours; this does not occur with rubber seed oil. Rubber seed oil and 25% of sulphur have been heated together at 150 — 160°C for about three to four days and even then there was no gel formation. It is believed that the presence of free fatty acids in the oil is the factor that prevents gel formation.

The use of different activators and accelerators in the manufacture of factice is well known (Roberts & Carrington, 1948). There are certain substances which catalyse the reaction of vulcanization between sulphur and oil, and they reduce the period necessary for gel formation and hardening, and at the same time reduce the temperature of the reaction.

Effect of accelerators : 100 g of rubber seed oil was heated with 25 g of sulphur with the addition of 1 g of mercaptobenzathiozole (MBT, the accelerator). The reaction mass became thick in 45 min. But on cooling only a semi-solid mass was formed. Post-treatment of this mixture with 5 g of sodium carbonate gave a dark solid product. Particles of Na_2CO_3 were visible.

Effect of zinc diethyldithiocarbomate (ZDC): Rubber seed oil (100 g), sulphur (25 g) and ZDC (1g) were heated to 140°C and zinc oxide (1g) was slowly added to the mixture ensuring that the temperature did not rise above 160°C. The temperature was maintained at 140°C — 160°C for 45 min. The product was cooled and left in the oven at 100°C for 24 hr. This resulted in a semi-solid mass.

Effect of activators : 100 g of rubber seed oil was tested with 25% sulphur, 1% MBT and 10% ZnO (activator). The temperature was raised to 160°C and external heating was then stopped. The reaction was exothermic and hence the temperature rose to 190°C. The product was then cooled and left in the oven at 100°C for 24 hr. A sticky semi-solid residue resulted.

The above procedure was repeated at 130°C adding 10% ZnO slowly, so that the temperature was kept below 160°C. The product obtained was quenched in water. On quenching it solidified but again it became a semi-solid mass at room temperature.

The sulphurization reaction can be modified by the use of bases and many claims have been put forward. Alexander & Pesnansky (G.P. 658128) and Posnansky & Sandvoss (B.P. 453921) have described the reaction of glyceride oils with sulphur and H_2S at temperatures lower than those normally used for dark factice in the presence of ammonia, amines and amides.

Attempts were made to prepare factice again with rubber seed oil and sulphur as above, with the addition of different percentages of ammonia, diphenylamine, NaOH and triethanol amine. But in all cases only a semi-solid sticky mass was formed (some products were soap-like).

Effect of pre-oxidation : It has been observed that for the preparation of factice, it is necessary to pass air through the oil initially, so that the density of the oil is brought to a certain fixed value (Anon, 1957). Here it is believed that a process of semi-oxidation across linkages is taking place.

100 g of rubber seed oil was placed in a cylinder and a jet of air was passed through it for 15 min at room temperature. Then the oil was heated up to 140°C in a nickel beaker and 25 g of sulphur and 10 g of Na_2CO_3 were added. Stirring was continued and the temperature was recorded every minute. The temperature rose to a maximum (Fig. 1) with the evolution of fumes and, while the temperature was descending from the maximum, the product turned into a hard gel and when the source of heat was removed it solidified quickly. The product was dark and very solid.

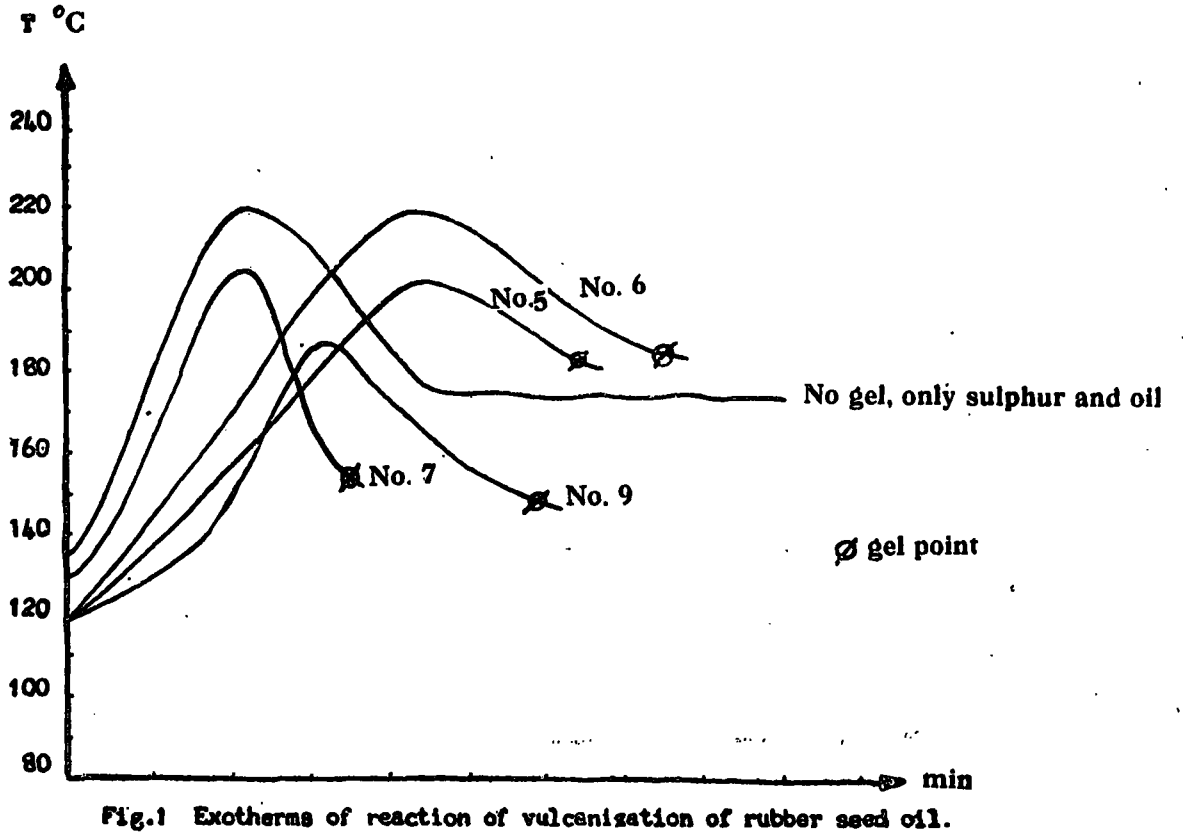


Fig.1 Exotherms of reaction of vulcanization of rubber seed oil.

Several other samples were tested with the same procedure using different proportions of sulphur and sodium carbonate. In all these cases satisfactorily hard products were formed.

Analysis of factice

The samples of factice formed were analysed for the amount of free unreacted oil by the acetone extract method and for the free sulphur content.

FREE SULPHUR AND ACETONE EXTRACT OF FACTICE PREPARED FROM RUBBER SEED OIL

Sample	% of sulphur	% of extract
5	0·3847	52·79
6	0·5696	36·10
7	0·2368	61·82
9	2·6048	54·22
10	2·6240	60·76

Sample
5. 100g rubber seed oil, 20% S, 10% Na_2CO_3 and air-blown at 150°C
6. 10% Na_2CO_3, 25% S, and air-blown initially at 150°C
7. 15% S, 10% Na_2CO_3 and air-blown initially at 150°C
9. 100 rubber seed oil, 10% Na_2CO_3, 25% S, not air-blown at 150°C
10. 100 rubber seed oil, 10% Na_2CO_3, 25% S, 1% diphenylamine.

Out of the experiments carried out it can be said that the best result was obtained with sample 6 formed from aerated rubber seed oil with 10% Na_2CO_3 and 25% S. The product is hard enough and is also prepared in a short time without the necessity of a secondary treatment as in the case with most other factices. The factice thus prepared is almost identical in properties to the calender factice of grade 790A made by the Anchor Chemical Company Limited. The product was dark in colour. A light colour could not be expected as it is vulcanized with sulphur and not with sulphur chloride, and the oil used itself was impure and very dark. The use of secondary alicyclic amines to reduce the colour was not tested, unfortunately due to the lack of chemicals.

White factice has already been produced successfully from rubber seed oil in Ceylon using sulphur chloride (Anon, 1957).

The factice produced in the above trials was used in manufacturing extruded rubber tubing on an experimental scale, and the compound containing 25% of the factice to 100% of smoked sheet gave very satisfactory results.

DISCUSSION

Though factice was manufactured successfully in a small scale, factors like (1) controlling the exotherm, and (2) toxicity of gaseous products, will have to be examined further before manufacturing on a large scale.

At present dark factice is imported into Ceylon from U.K. for essential purposes. Some manufacturers do not use factice, although it is essential because it involves foreign exchange. So if the necessary dark factice is prepared in Ceylon, making use of our own rubber seed oil with very inexpensive chemicals like sulphur, and Na_2CO_3 using very simple technology, a considerable amount of foreign exchange can be saved and this will also assist to some extent in solving the employment problem too (*e.g.* collection of rubber seed and extraction).

The samples of factice produced at the Dartonfield laboratories have been given to Associated Motorways Limited for experimental purposes.

ACKNOWLEDGEMENT

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