

EXAMINATION OF RUBBERSEED OIL FOR USE IN COATING COMPOSITIONS

MOHAMMAD ASLAM AND HASSAN IMAM

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

Introduction

Rubberseed oil is obtained from the seeds of *Hevea Brasiliensis*, native to Brazil and extensively cultivated in many tropical regions including Malaya, Borneo, Sumatra and Ceylon. The yield of the seed is estimated at 300 lbs./acre/annum. The total area under rubber cultivation in the various rubber producing countries of the world was reported¹ to be 10,000,000 acres in 1953, so that the potential availability of seeds would be about 1.3 million tons annually, making for a total of 260,000 tons of the oil on the basis of 20% yield. As against this potential, the present world output of the oil is reported to be only 20,000 tons, corresponding to a 8% utilisation of the seeds.

There are two main reasons for this neglect of such a valuable source of oil :

(1) The seeds deteriorate rapidly on storage, yielding a dark-coloured oil with a high proportion of free fatty acids. To counteract this drawback, various methods of heat treatment have been suggested, and it is reported^{2,3} that the seeds do not deteriorate and the oil extracted from heat-treated seeds can be stored for as long as two years with very little increase in free acidity.

(2) Lack of economic methods for improving the drying properties of semi-drying oils like rubberseed oil or for using them in oleo-resinous varnishes. Fatty acids obtained from semi-drying oils are no doubt favoured for the preparation of alkyd resins, but their present demand is being largely met by another semi-drying oil, namely soyabean oil. The present output of rubberseed oil appears to be mostly consumed in soap manufacture, though it has also been recommended, as an adulterant for linseed oil and as its substitute in core binders.⁴

In order to gauge the drying power of an oil for use in coatings, a drying index has been suggested⁵ in the form of the sum of the percentage content of linoleic acid and double the percentage content of linolenic acid. Drying indices calculated on this basis for linseed, rubberseed, soyabean and cottonseed oils work out to be 120, 80, 68 and 45 respectively. The drying properties of rubberseed oil can therefore be regarded as being intermediate between those of soyabean and linseed oil, and it would therefore be ad-

vantageous to study its utilization in coating compositions. In view of the fact that rubber plantation has been recently started in East Pakistan, it was considered of importance to undertake a fuller investigation of the various aspects of the problems relating to the utilisation of the rubberseed in order to strengthen the economy of the plantation. The present paper deals with the results of studies in the keeping quality of the seeds and the extracted oil, both with and without heat treatment, and the utilisation of the oil for the preparation of oleo-resinous varnishes capable of giving tack-free films with the process developed for cottonseed oil⁶ at the Central Laboratories. For the present study, the rubberseeds were obtained from Malaya through Messrs Chemtong Malaya Rubber Company, soon after collection.

Experimental

The seeds were found to contain 41.8% shell and 58.2% kernel, the latter containing 37% oil. The moisture content of the kernel was 7.8% by weight and 8.0% by weight in the whole seeds. The characteristic constants of the oil from the seeds as received were measured and are reported in Table I. The reported values show large variations, which are probably due to variations in age and quality of the rubberseeds.

Detailed examination showed that rubberseeds exhibit considerable variations in quality and the seeds were therefore classified according to the colour of the kernel as given in Table 2, the oil from the dark varieties having a much higher acid value than that from the light varieties.

Uncorticated seeds, without heat treatment and after heat treatment for varying periods, were stored in tin cans. At six-monthly intervals, the oil was extracted from these stored seeds using petroleum ether as a solvent and its content of free fatty acid was determined in order to estimate the rate of deterioration of the seeds. The results are reported in Table 3.

To study the storage deterioration further, the oil from the two main varieties, light and dark, was extracted and its keeping qualities were compared with the oil from the total rubberseeds during storage for about 15 months. The acid values determined at different intervals are given in Table 4.

TABLE 1.—CHARACTERISTIC CONSTANTS OF RUBBERSEED OIL.

		Present Investigation	Ref. 7	Ref. 8	Ref. 9
Specific gravity at 26°C.	..	0.9178	—	{ 0.9245 at 15°C.	0.924— 0.930 at 15°C.
Refractive index at 26°C.	..	1.4723	—	—	{ 1.4665— 1.4685 at 40°C.
Acid value	..	22.6	40.9	—	10—50
Iodine value (Hanus)	..	132.2	135.2	139.3	133—143
Saponification value	..	209	191.8	192.5	186—195
Unaponifiable matter %	..	1.3	—	—	0.5—0.8

TABLE 2.—CLASSIFICATION OF RUBBERSEEDS AS RECEIVED.

Colour of Kernel		Proportion %	Oil content (on weight of kernel) %	Colour of oil	Acid value	
Light	{ White	..	20.0	38.8	faint yellow	2.9
	{ Cream	..	50.0	38.5	yellow	4.6
Dark	{ Dirty brown	..	25.0	33.2	reddish brown	60.9
	{ Grey black	..	5.0	30.6	dark brown	86.2

TABLE 4.—ACID VALUES OF STORED OILS FROM THE RUBBER SEEDS.

Date of examination			Oil from light seeds (untreated)	Oil from light seeds (heat treated)*	Oil from dark seeds	Oil from total rubber seeds
5- 1-57	4.1	3.9	64.6	22.6
16- 1-57	4.2	4.1	66.8	23.0
16- 2-57	4.4	4.2	76.9	24.6
17- 4-57	4.6	4.5	89.6	30.4
16- 6-57	5.1	5.2	96.8	35.2
14-10-57	6.2	7.3	†	
31- 3-58	7.2	23.0		42.7

* Kernels heated at 100°C. for one minute.

† Acid value remains constant, but free fatty acids keep depositing.

It was observed that, oil from heat treated kernels showed a slow increase in viscosity from 42 centistokes at 25°C. to 60 centistokes at 25°C. during the first nine months and thereafter a sharp increase, the viscosity after fourteen months' storage being found to be 450 centistokes at 25°C. During this latter period, the acid value also showed a sharp increase, the two effects indicating polymerization of the oil. On the other hand,

the oil from untreated kernels retained the original viscosity on storage. Separation of free fatty acids started in the oil from the dark varieties after storage of three months, and after fifteen months the iodine value of the supernatant oil had increased to 135.5. There was no separation of free fatty acids in the other varieties.

TABLE 3.—ACID VALUES OF OILS FROM STORED SEEDS WITH AND WITHOUT HEAT TREATMENT.

Period of storage	Untreated	Seeds heated at 100°C. for (in minutes)		
		5	10	20
Initial	22.5	—	—	—
6 months	82.5	35.6	33.8	34.2
12 "	—	38.6	37.9	38.0
18 "	—	46.8	42.7	43.3

A process developed at the Central Laboratories for preparing tack-free coatings (oleo-resinous) from cottonseed oil (iodine value 107), has now

TABLE 5.—COMPARATIVE SCRATCH TEST OF VARNISH FILMS.

Sl. No.	Oil length (gallons)	Load in grams	
		Rubber-seed varnish	Linseed varnish
Initial	22.5	—	—
6 months	82.5	35.6	33.8
12 "	—	38.6	37.9
18 "	—	46.8	42.7

TABLE 6.—COMPARATIVE WATER RESISTANCE OF VARNISH FILMS.

Sl. No.	Oil length	Oil used	Water-resistance of films				
			1 hr.	2 hrs.	4 hrs.	24 hrs.	48 hrs.
1	15	Rubberseed	.. OK	OK	V. Sl. H.	Sl. H. (D : 2 hrs.)	W (D : 16 hrs.)
	15	Linseed	.. OK	OK	OK	Sl. H. (D : 2 hrs.)	W (D : 14 hrs.)
2	25	Rubberseed	.. OK	V. Sl. H. (D : 5 mins.)	Sl. H. (D : 45 mins.)	H (D : 24 mins.)	P. W.
	25	Linseed	.. OK	OK	V. Sl. H. (D : 20 mins.)	H (D : 80 mins.)	P. W.
3	35	Rubberseed	.. H (D : 3 hrs.)	V. H. (D : 8 hrs.)	W (D. N. D.)	P. W. (D. N. D.)	
	35	Linseed	.. OK	Sl. H. (D : 2 hrs.)	H (D : 24 hrs.)	P. W. (D N D)	

OK = Satisfactory, Sl. = Slight, D = time taken for haze to disappear, W = Whiteness, H = hazy, V. Sl. = Very slight, D.N.D. = Does not disappear, P.W. = Pronounced whiteness, V.H. = very hazy.

been extended to rubberseed oil (iodine value 132). In this case it has been found possible to prepare tack-free oleo-resinous varnishes upto an "oil length" of $37\frac{1}{2}$ gallons as against 18 gallons in the case of cotton-seed oil. (Oil length signifies gallons of oil per 100 lbs. of resin.) Any further increase in the proportion of the oil was found to result in tacky finishes. It was further observed that oil containing high proportion of free fatty acids can also be utilised, if the formulation includes a sufficient excess of glycerol for esterifying the free fatty acids.

Oleo-resinous varnishes of '15', '25' and '35' gallon oil length based on rubberseed oil were prepared and their properties compared with similar varnishes made from linseed oil. For the purpose of testing, all the varnishes were adjusted to viscosity E (Gardner-Holdt), then applied on carefully cleaned tin panels, and allowed to air-dry for seven days. The scratch resistance of the films was evaluated by determining the loads required for rupturing films on standard scratch test apparatus. The results are reported in Table 5.

The water-resistance of the air-dried films was evaluated by dipping the panels in water for periods of 1, 2, 4, 24 and 48 hours. The results are reported in Table 6.

Conclusions

From the foregoing experiments it may be concluded that heat treatment of the seeds does slow down the deterioration, though it does not completely prevent it. The oil extracted from white and cream varieties by solvent extraction

has excellent keeping qualities. Rubberseed oil can be used as such for preparing tack-free finishes, which compare favourably with similar varnishes prepared from linseed oil.

Further studies with special reference to the polymerisation of the oil from heated kernels is in progress.

Acknowledgements

The authors are grateful to Dr. Salimuzzaman Siddiqui for suggesting this problem and for his continued interest, and to Mr. Ali Hussain for helping with some of the experimental work. The authors gratefully acknowledge the help rendered by UNESCO in supplying a comprehensive bibliography.

References

1. *Encyclopedia Chemical Technology*, Vol. II, p. 811.
2. T.P. Hilditch, *J. Oil and Colour Chemists' Assoc.*, **32**, 5-32 (1949).
3. C.D.V. Georgietell, *Malayan Agr. J.*, **20**, 164-76 (1932).
4. L.W. Greve and J.M. Faraday, *Oil and Soap*, **10**, No. 1 28-29 (1933).
5. G.H. Greaves, *Oil and Colour Trades J.*, **113**, 949 (1948).
6. S. Siddiqui and M. Aslam, *Indian Patent* 60,100 (April 3, 1957).
7. Jamieson and Barghman, *Oil and Fat Ind.*, **7**, 419 (1930).
8. B.J. Eaton, *Bull. Imp. Inst.*, 156 (1903).
9. Jamieson, *Vegetable Fats and Oils* (Reinhold Publishing Corp., 1943), p. 295.