Natural Rubber Research, 17(2) : 159-167, 2004

STUDIES ON COPPER SOAP OF RUBBER SEED OIL AS PEPTIZER FOR ESTIMATION OF DIRT CONTENT IN NATURAL RUBBER

Reethamma Joseph, Rosamma Alex, Ramesh B. Nair, C.K. Premalatha and Baby Kuriakose
Rubber Research Institute of India, Kottayam – 686009, Kerala, India.

Submitted: 20 October 2003 *Accepted: 31 December 2004*

Joseph, R., Alex, R., Nair, R.B., Premalatha, C.K. and Kuriakose, B. (2004). Studies on copper soap of rubber seed oil as peptizer for estimation of dirt content in natural rubber. *Natural Rubber Research*, 17(2) : 159-167.

Dirt content is one of the important quality parameters specified in the grading of technically specified rubber (TSR). It is estimated by dissolving rubber in a solvent with the aid of a peptizer, such as copper oleate and then determining the weight of dry matter retained on a standard sieve, when the solution is filtered. The performance of copper soap of mixed fatty acids, prepared from rubber seed oil, was evaluated for the estimation of dirt content of TSR in comparison with that of copper oleate. The results indicated that mixed fatty acid soaps of copper prepared from rubber seed oil is as good as copper oleate for the purpose and is a cheaper alternative.

Key words : Dirt content, Peptizer, Rubber seed oil, Technically specified rubber.

INTRODUCTION

The seeds of rubber tree (*Hevea brasiliensis*), the major source of natural rubber, have been found to be rich in oil (Potty, 1980; Haridasan, 1992; Thomas *et al.*, 1996). Rubber seed is an important by-product obtained from rubber tree and it contains about 65 per cent kernel and 35 per cent shell (Pillai and Wijewantha, 1967). The dried kernel contains about 42 per cent oil (Pickles *et al.*, 1911; Azeemoddin and Rao, 1962; Uzu *et al.*, 1986; Attah *et al.*, 1990), which is extracted by expulsion process. Fresh rubber seed oil (RSO) is a light yellow coloured semidrying oil, and contains about 18-22 per cent saturated and 78-82 per cent unsaturated higher fatty acids (Bressani *et al.*, 1983).

There are many industrial applications for RSO. It is used for the production of factice (Vijayagopalan, 1971). Epoxidised rubber seed oil (ERSO) (Vijayagopalan and Gopalakrishnan, 1971) is used in formulations for anticorrosive coating, adhesive and for alkyd resin coating (Aigbodion, 1994). Properties of RSO resemble linseed oil and hence has a strong potential for replacing linseed oil, wholly or partially, in alkyd resin production (Aigbodion, 1991). Use of RSO, ERSO and its lead and barium soaps as heat stabilizers for PVC has been reported from Nigeria (Okieimen and Ebhoaye, 1992, 1993). RSO and ERSO can be used in natural rubber compounds for improving their processability and physico-mechanical properties (Aigbodion *et al.*, 2000). RSO contains higher fatty acids and can be used for the preparation of soap (Haridasan, 1977).

Quality of technically specified rubber (TSR) is related to both processing and technical parameters. Wallace initial plas-

Correspondence: Reethamma Joseph (Email: rrii@rubberboard.org.in)

ticity (P_0) and plasticity retention index (PRI) are related to compound viscosity and ageing resistance respectively. Another important parameter is dirt content, which affect the technological properties of TSR such as tensile strength, tear strength DIN abrasion and flex crack resistance. Dirt content in rubber is defined as particles of foreign matter and the natural serum substances, which can be separated from rubber by physical methods. The dirt present in NR acts as initiation points of cracks, which grow during repeated stress under tension, compression etc., leading to failure of the material. According to Bristow and Greensmith (1973), when dirt content increases, tensile strength and fatigue life of rubber decrease.

Wide variations have been observed in dirt content values of identical raw rubber samples tested in different laboratories in spite of using similar test procedures (Nair *et al.*, 1972; Ehabe and Sainte-Beauve, 2001). Martin (1950) suggested visual examination of sheet under polarised light as the dirt particles, which are not clearly seen in normal light, also show up under it.

Different procedures for estimating the dirt content of raw rubber have been developed over the years. These include a method based on ash content determination which is reported to be not very reliable (Heinisch and Van der Bie, 1951) and the washing method suggested by Frank (1934) and the American Chemical Society (1940). These methods can be regarded only as approximate industrial test methods. The absolute values cannot be estimated by washing methods as even after vigorous washing fine particles of sand, wood, bark and fibres are observed to be left in the rubber (Bekkedahl, 1947).

A sufficiently accurate gravimetric estimation of harmful dirt can be made quickly by the dissolution method. This method involves dissolving raw rubber in a hydrocarbon solvent to obtain a homogeneous and low viscosity solution. The solution is sieved and the dirt retained is dried and weighed. This process can be accelerated by oxygen-carriers that reduce the dissolution temperature (Heinisch and Van der Bie, 1951). Free radicals formed by mechanical, thermal and chemical bond scission of crude rubber in solution are stabilized by recombining in pairs, or on sites along the rubber chain to give branched species. The presence of a peptizer (eg. xylyl mercaptan) or an oxidation activator (like cobalt naphthenate) in the solution inhibits the recombination process by reacting rapidly with the free radicals. Addition of hydrogen peroxide to mercaptan solution also slightly inhibits recombination. The accuracy of this method depends on the rubber solution of a very low viscosity from which the insoluble part can be easily separated by a suitable process like filtering or centrifuging.

The method proposed by the American Chemical Society (1941) consisted of dissolving rubber in para-cymene to which an oxidising agent (H_2O_2) was added. Addition of oxygen carrier accelerates the process and reduces the temperature of dissolution. Hublin (1946) studied the use of other solvents and reported ortho-nitroanisole as the best as it dissolved the rubber within 20-60 minutes at 100-200 °C.

Rubber can be dissolved in toluene in the presence of 1 per cent trichloro acetic acid (Bekkedahl, 1947), copper oleate (Van Essen, 1950) or stannous chloride (Kahn, 1950). Among the different peptizers

RPA 3 was reported as the most effective (Heinish and Van der Bie, 1951) and addition of strong electrolytes like HCl further reduced the viscosity of the rubber solution. Kerosene was also observed as a good solvent for rubber and copper oleate was reported as effective as RPA 3 in reducing viscosity of the rubber solution (Kuriakose *et al.,* 1976) for gravimetric estimation of harmful dirt that is retained on a 325 mesh sieve (IS : 460 (part I), 1985). Copper also acts as a pro-oxidant to break the double bonds in natural rubber. Such chain scission accelerates the dissolution of rubber.

Dirt content in the processed rubber is currently estimated by dissolving rubber in a solvent with the aid of a peptizer, such as copper oleate and then filtering the solution through a standard stainless steel sieve (IS: 3660: 1999; ISO 249: 1995 (E)). Latex grade TSR and sheet rubber required longer time of heating for getting a clear homogeneous solution. After a critical dissolution time, further heating leads to the formation of macrogel that remains insoluble in most of the non-polar hydrocarbon solvents, which results in poor repeatability of dirt values (Ehabe and Sainte-Beauve, 2001).

This study was conducted to evaluate the performance of rubber seed oil (which contains about 24 per cent oleic acid and other fatty acids) as a substitute for oleic acid to prepare the copper soap for the estimation of dirt content of rubber.

MATERIALS AND METHODS

Rubber seed oil was obtained from commercial sources. The fatty acid composition of the oil was analysed using Waters Gel Permeation Chromatography (GPC). RSO (10 g) was heated in a water bath at 80°C and to it 2.5 g of potassium hydroxide dissolved in 40 ml of water was added and stirred well. The RSO soap formed was acidified to pH 2 with dilute HCl. The acidified aqueous solution was then extracted with 50 ml of ether using a separating funnel. The lower aqueous layer was drained out and re-extracted three times with 30 ml of ether each time, the extracts combined and evaporated on a water bath. The residue was dissolved in 20 ml of solvent (HPLC grade) mixture prepared at the ratio 45:35:25 using acetonitrile, water and tetrahydro furan respectively.

Standard calibration graphs were drawn using pure acids (as 0.1% solution) in the solvent mixture and the unknown samples were analysed using the liquid chromatogram (LC programme). The physical properties of RSO were determined as per the Association of Official Analytical Chemists (AOAC) method. All other chemicals used were of laboratory reagent grade.

For preparing copper oleate from oleic acid and mixed oleate from rubber seed oil, 14 g of potassium hydroxide was dissolved in 140 ml of distilled water and slowly added to 70.5 g of warm oleic acid / rubber seed oil and 190 ml of water in a beaker. The solution was stirred vigorously while adding potassium hydroxide. Copper sulphate (31.2 g) was dissolved in 200 ml of water and added to the above hot solution, stirred and heated at 90°C for 1 h and kept overnight. The copper soap formed was washed three times with water, drained, dissolved in ether and transferred into a separating funnel. The ether layer was collected and evaporated. The copper soap separated was diluted four times with mineral turpentine and filtered through a 325 mesh sieve.

Since ISNR 5 and ISNR 20 are the most common TSR grades processed in India from latex and field coagulum materials respectively, the effect of the peptizer was evaluated for the estimation of dirt content of these grades only. The experiment was carried out in a statistical design, using 20 samples each of ISNR 5 and ISNR 20, collected from different sources. Three concentrations (0.5, 1.0 and 1.5 ml of 25% solution) of copper soaps of mixed fatty acids from rubber seed oil were compared with copper oleate (1.0 ml of 25% solution) for the estimation of dirt content. 200 ml of mineral turpentine was used as solvent for each treatment.

The rubber samples for the determination of dirt content were drawn as per IS 5599: 1970; ISO 1795: 1992 and homogenized by passing six times in a two-roll mill rotating at a friction ratio of 1:1.25 and a nip gap set at 1.65 mm. The rolls were cooled with running water at room temperature. The homogenized rubber (60g) was passed twice through a cold mill with 1.3 mm nip setting. The sheeted out rubber, cut into small pieces, was used for the estimation of dirt content.

The viscosity of the rubber solutions prepared using copper oleate and copper soaps of higher fatty acids from rubber seed oil as peptizers (the first filtrate from the dirt content estimation) was determined using a 'Haake' Viscotester (VT-550). Nine ml of the solution, which contained varying concentrations of copper oleate/copper soap of rubber seed oil as peptizer, was tested using the viscometer. The temperature was set at a definite value in the range of 40 to 70 °C and the speed of rotation was varied to get shear rates ranging from 1 to 200 per second. From the data obtained, the viscosity values of the solution at different temperatures and shear rates were calculated.

For estimating the dirt content, about 10 g of the homogenised rubber was accurately weighed, cut into small strips and soaked in 200 ml of mineral turpentine (low aromatic petroleum hydrocarbon solvent) containing 1 ml of 25 per cent copper oleate solution in a 500 ml conical flask (control). The experiment was carried out using 0.5, 1.0 and 1.5 ml of 25 per cent solution of copper soap of higher fatty acids prepared from RSO. The rubber was allowed to swell over-night and heated at 125 to 130 °C for 5 h on the following day. A short air condenser was fitted and the flask was shaken occasionally during heating (IS: 3660 part I: 1999). Infrared lamps were used for heating as it minimised the formation of gel and consequent filtration difficulties as well as over heating or boiling, which caused gelling/charring. When the rubber was completely dissolved, the solution was filtered through previously weighed, clean and dry 325 mesh stainless steel sieve. The filtrate was collected in clean dry filtering flask and a portion of this final filtrate was separately earmarked for viscosity studies. The flask was washed 3 or 4 times with 20 to 30 ml of hot (40 to 50 °C) mineral turpentine and the washings also were filtered through the same sieve.

The dirt in the sieve was washed by using a jet of hot solvent until it was free from rubber. The sieve with the dirt was then dried in an air oven at 100 ± 2 °C for 30 minutes and transferred to a desiccator, cooled and weighed. Drying, cooling and weighing were continued till constant mass (to the nearest 0.1 mg) was obtained. Five replications were maintained for each set of samples. The dirt content was calculated by the following formula:

$$\text{Dirt content, percent by mass} = \frac{m_1}{m_2} \times 100$$

where m_1 = mass (g) of the dirt and
m_2 = mass (g) of the rubber sample

For estimating the dirt content, the standard method was compared with 3 treatments M1, M2 and M3 containing 0.5, 1.0 and 1.5 ml respectively of copper soap of mixed fatty acids prepared from rubber seed oil. While selecting the samples of ISNR 5 and ISNR 20, care was taken to cover a wider range of dirt values (eg: 0.009 to 0.048% for ISNR 5 and 0.083 to 0.199% for ISNR 20) within each grade. Each dirt content value reported was the average of five determinations.

RESULTS AND DISCUSSION

The fatty acid composition of RSO is presented in Fig. 1. The results were comparable to the composition earlier reported for RSO (Bressani *et al.*, 1983) using AOAC test method. The physical properties of RSO are given in Table 1. The iodine value of 132 confirms that RSO is an unsaturated and semidrying vegetable oil. Tables 2 and 3 contain the dirt content values recorded for 20 different samples of ISNR 20 and ISNR 5 respectively. These values are the average of five replications. From Table 4 it could be observed that the percentage dirt content values obtained for ISNR 20 and ISNR 5 using copper soap of RSO at concentration of 0.5 ml, 1 ml and 1.5 ml of 25 per cent solution of the copper soap of RSO, were comparable to those of the control (i.e. 1 ml of copper oleate) as is indicated by the mean, standard deviation and t values. The deviation in the values of dirt content of the experimental samples from those of the control was not significant statistically indicating that these concentrations of copper soap obtained from RSO could be used for the determination of dirt content without affecting the accuracy of the test results. However, from a practical point of view 1.0 ml of 25 per cent copper soap of mixed fatty acids

Table 1. **Physical properties of rubber seed oil**

Parameter	Value
Acid value	36
Saponification value	191
Iodine value	132
Hydroxyl value	31
Unsaponifiables (%)	0.80
Refractive index (40°C)	1.47
Specific gravity (30°C)	0.92
Titre (°C)	28

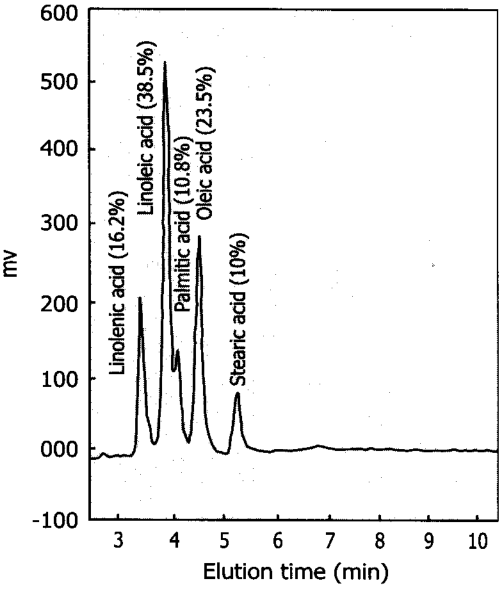

Fig. 1. Liquid chromatogram of RSO showing fatty acid profile

Table 2. **Dirt content (%) of ISNR 20**

Sample No.	C	M1	M2	M3
1	0.198	0.195	0.196	0.200
2	0.096	0.098	0.096	0.099
3	0.095	0.092	0.094	0.099
4	0.093	0.092	0.093	0.097
5	0.099	0.093	0.098	0.095
6	0.092	0.094	0.093	0.095
7	0.118	0.116	0.118	0.120
8	0.088	0.092	0.089	0.113
9	0.125	0.122	0.125	0.126
10	0.111	0.107	0.111	0.108
11	0.083	0.082	0.083	0.084
12	0.155	0.155	0.155	0.157
13	0.199	0.195	0.198	0.195
14	0.127	0.124	0.127	0.128
15	0.110	0.111	0.110	0.111
16	0.099	0.101	0.099	0.098
17	0.122	0.123	0.122	0.121
18	0.150	0.151	0.150	0.151
19	0.183	0.185	0.183	0.183
20	0.139	0.142	0.139	0.138

C = Control; M_1, M_2, M_3 contain 0.5, 1.0 and 1.5 ml of 25% solution of copper soap of RSO respectively

Table 3. **Dirt content (%) of ISNR 5**

Sample No.	C	M1	M2	M3
1	0.031	0.029	0.032	0.040
2	0.042	0.028	0.042	0.041
3	0.010	0.011	0.010	0.011
4	0.015	0.014	0.016	0.015
5	0.034	0.035	0.035	0.034
6	0.016	0.017	0.016	0.018
7	0.030	0.028	0.030	0.030
8	0.028	0.029	0.027	0.028
9	0.023	0.022	0.023	0.023
10	0.029	0.028	0.029	0.031
11	0.013	0.012	0.013	0.013
12	0.011	0.015	0.011	0.011
13	0.048	0.049	0.048	0.049
14	0.025	0.026	0.025	0.027
15	0.024	0.025	0.024	0.027
16	0.009	0.009	0.010	0.111
17	0.020	0.020	0.020	0.020
18	0.024	0.023	0.024	0.024
19	0.030	0.031	0.030	0.031
20	0.018	0.018	0.018	0.018

C = Control; M_1, M_2, M_3 contain 0.5, 1.0 and 1.5 ml of 25% solution of copper soap of RSO respectively

appears to be the ideal concentration of this peptizer, as higher concentrations can lead to the formation of macrogel. There is a saving of about 32 per cent on the cost of peptizer when copper soap of RSO is used instead of copper oleate.

The plots of viscosity in relation to shear rate for the rubber solutions containing 1.0 ml of 25 per cent solution of copper oleate (control) and 1.0 ml and 1.5 ml of 25 per cent solution of copper soap of RSO, at 70 °C are presented in Fig. 2. It is evident that the viscosity of the solution containing 1.0 ml of copper soap solution from

Table 4. **Statistical significance of dirt content values**

Treatment	Differences			
	Mean	SD	t value	Significance
ISNR 20				
Standard vs M1	0.00055	0.00346	0.71169	NS
Standard vs M2	-0.00015	0.00049	0.02267	NS
Standard vs M3	-0.00610	-1.37081	-1.20328	NS
ISNR 5				
Standard vs M1	0.00060	0.00278	0.96534	NS
Standard vs M2	0.00015	0.00067	1.00000	NS
Standard vs M3	-0.00018	0.00594	-1.35437	NS

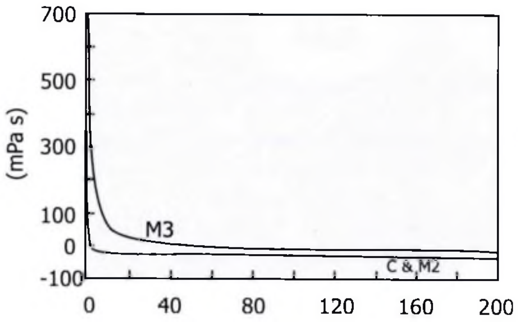

Fig. 2. Viscosity vs shear rate plots of solutions of ISNR 20 containing peptizer at 70 °C. M3: 1.5 RSO. C: 1 ml control. M2: 1 ml RSO

RSO is comparable to that of the control, which contained 1.0 ml of copper oleate solution at all shear rates. However, the solution, which contained a higher concentration of the copper soap (1.5 ml) showed comparatively higher viscosity values than the control. This may be due to the formation of macrogel in the solution. It has been reported that a higher concentration of peptizer or prolonged heating at a higher temperature leads to macrogel formation (Ehabe and Sainte-Beauve, 2001).

The effect of temperature on the viscosity of the solutions containing 1.0 ml of copper oleate and 1.0 ml of copper soap of RSO, at a shear rate of 20 per second is shown in Fig. 3. The viscosity decreased with increase in temperature. At 70 °C, the viscosity values of the control and that of the sample containing 1 ml of copper soap of RSO were the same. However, at lower temperature the solution containing the copper soap of RSO had lower viscosity values. This is advantageous in dirt estimation for quick filtration of the solution through the sieve, even if the temperature is slightly lower.

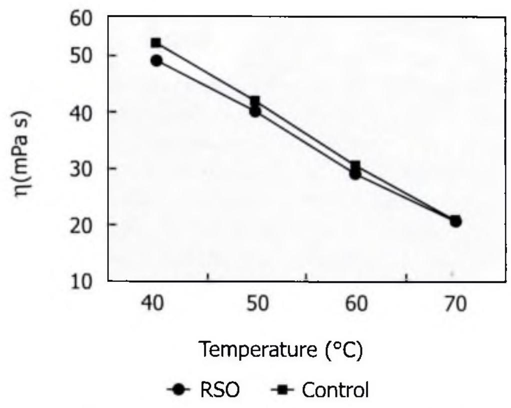

Fig. 3. Viscosity vs temperature plots for solutions of ISNR 20 containing 10 ml peptizer at shear rate of 20 S^{-1}

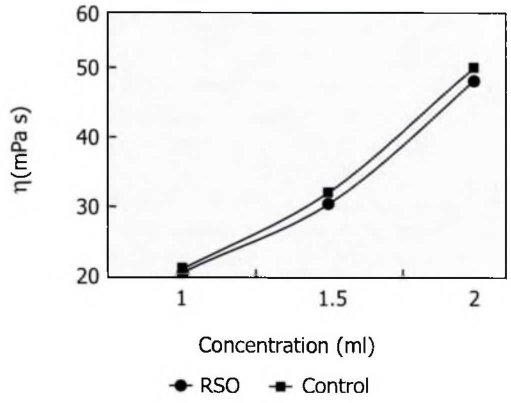

Fig. 4. Viscosity vs concentration of peptizer plots of solutions of ISNR 20 at 20 S^{-1} at 70 °C

The plots of viscosity against concentration of peptizer at a shear rate of 20 per second and a temperature of 70 °C is shown in Fig. 4. It was observed that higher concentrations of either copper oleate or copper soap of RSO increased the viscosity at that shear rate. Both the solutions had the same viscosity when the dosage of peptizer was 1.0 ml. This may be due to the formation of macrogel, which increases the viscosity of the rubber solution when higher concentration of peptizer was used. Solutions of both ISNR 5 and ISNR 20 showed the same trend in such evaluations.

REFERENCES

Aigbodion, A. I. (1991). Preliminary studies on the preparation of rubber seed oil alkyds. *Indian Journal of Natural Rubber Research,* **4**(2): 114-117.

Aigbodion, A. I. (1994). Effect of storage of seeds on quality of rubber seed oil. *Indian Journal of Natural Rubber Research,* **7**(2): 141-143.

Aigbodion, A. I; Menon, A. R .R. and Pillai, C. K. S. (2000). Processability characteristics and physico-mechanical properties of natural rubber modified with rubber seed oil and epoxidized rubber seed oil. *Journal of Applied Polymer Science,* **77**: 1413-1418.

American Chemical Society (1940). Report. Crude Rubber Committee. *Rubber Chemistry and Technology,* **13** : 441.

American Chemical Society (1941). Report. Crude Rubber Committee. *Rubber Chemistry and Technology,* **14** : 295.

Attah, J. C. and Ibemesi, J. A. (1990). Solvent extraction of the oils of rubber, melon, pumpkin and oil bean seeds. *Journal of American Oil Chemists Society,* **67**(1): 25-27.

Azeemoddin, G. and Rao, S. D. T. (1962). Rubber seed and oil. Studies on Indian rubber seed and rubber seed oil: 1. Availability of seed, characteristics and composition of seed and oil. *Rubber Board Bulletin,* **6**(2): 59-68.

Bekkedahl. (1947). Testing and grading of wild and plantation rubber. *Rubber Age,* **62**: 173.

Bressani, R., Elias, L. G, Ayuso, T., Rosal, O., Braham, J. E. and Zuniga, J. (1983). Nutritional value of protein and oil in rubber seed *(Hevea brasiliensis). Turrialba,* **33**(1): 61-63.

Bristow, G. M and Greensmith, H. W. (1973). Technical survey of SMR and competing NR grades. Summary report on first phase results, 1970/1972. Malaysian Rubber Research and Development Board, Hertfordshire, U K , 1973.

Ehabe, E. S. and Sainte-Beauve, J. (2001). Factors affecting the estimation of dirt content in raw natural rubber. *Indian Journal of Natural Rubber Research,* **14**(1): 30-35.

Frank, F. (1934). Kautschuk and Kautschuk waren. In: *Berl-Lunge: Chemical Technology.* Untersuchungsmethoden, Vol. 5, Berlin, p. 445.

Haridasan, V. (1977). Utilisation of rubber seed oil in India. *Rubber Board Bulletin,* **12**(1&2):19-24.

Haridasan, V. (1992). Ancillary income from rubber plantations. In: *Natural Rubber: Biology, Cultivation and Technology* (Eds.M.R. Sethuraj and N.M. Mathew), Elsevier Scientific Publishers, Amsterdam, p 561.

Heinisch, K. F. and Van der Bie, G. J. (1951). Dirt content of crude *Hevea* rubber: 1. Determination of dirt content. *Archiefvoor de Rubber Culture,* **28**(1): 1-15.

Hublin, R. A. (1946). New method for filler content of vulcanised rubber. *Rubber Chemistry and Technology,* **19**: 482.

IS: 460(Part I: 1985). Test sieves: 1. Wire cloth test sieves (Third Revision). Bureau of Indian Standards, New Delhi.

IS: 3660 (Part I: 1999). Methods of test for natural rubber: I. Determination of dirt (Third Revision). Bureau of Indian Standards, New Delhi.

IS: 5599 (1970). Methods of sampling of raw rubber. Bureau of Indian Standards, New Delhi.

ISO 1975 (1992). Rubber, raw natural and synthetic – sampling: International Organisation for Standardisation, Geneva.

ISO 249 (1995 (E)). Rubber, raw natural: Determination of dirt content. International Organisation for Standardisation, Geneva.

Kahn (1950). American Society for Testing Materials, Third Meeting Sub-committee. XII, Crude Natural Rubber, ASTM Committee D-II on Rubber and Rubber Like Materials, October 14, Akron.

Kuriakose, A. P., Peethambaran, N.R. and Thomas, E. V. (1979). Standardisation of a solvent and a peptizer for the dirt content estimation in *Hevea* rubber. *Proceedings of the IRRDB Meeting,* 8-9 November, 1979, Bogor, Indonesia. Paper No:7.

Martin (1950). American Society for Testing Materials, Third Meeting of Sub-committee. XII, Crude Natural Rubber, ASTM Committee D-II on Rubber and Rubber Like Materials, October 14, Akron.

Nair, K.S., Wong, L. and Mum, L. (1972). SMR and its control. Technical Report, Rubber Research Institute of Malaysia, Kuala Lumpur, 70p.

Okieimen, F. E. and Ebhoaye, J. E. (1992). Thermal dehydrochlorination of PVC in the presence of metal soaps derived from rubber seed oil. *European Polymer Journal,* **28**: 1423-1425.

Okieimen, F. E. and Ebhoaye, J. E. (1993). Studies on the thermal degradation of polyvinyl chloride. *Journal of Applied Polymer Science*, **48**: 1853-1858.

Okieimen, F. E. and Ebhoaye, J. E. (1993). Thermal dehydrochlorination of PVC in the presence of rubber seed oil. *Angewandte Makromolekulare Chemie*, **206**: 11-20.

Pickles, S. S. and Hayworth, W. P. (1911). Composition of Para-rubber seed oil, *Analyst*, **36**: 491-492.

Pillai, N.N. and Wijewantha, R. T. (1967). Productivity potentials of rubber seed. *Rubber Research Institute of Ceylon Bulletin*, **2**: 8-17.

Potty, S. N. (1980). Nursery establishment and field planting. In: *Handbook of Natural Rubber Production in India* (Ed. P.N Radhakrishna Pillai), Rubber Research Institute of India, Kottayam, pp 113-130.

Thomas, V., Mercykutty, V. C. and Saraswathyamma, C. K. (1996). Seed biology of para rubber tree (*Hevea brasiliensis Muell. Arg., Euphorbiaceae*): A review. *Phytomorphology*, **46**(4): 335-342.

Uzu, F. O., Ihenyen, G. A. and Imoebe, S. O. (1986). Processing, analysis and utilization of rubber (*Hevea brasiliensis*) seed oil and cake. In: *Industrial Utilization of Natural Rubber (Hevea brasiliensis) Seed, Latex and Wood* (Ed. E. E. Enabor), Rubber Research Institute of Nigeria, Benin City, pp.19-26.

Van Essen, W. J. (1950). Rapid determination of the content of dirt in rubber. *Journal of Rubber Research Institute of Malaya*, **12**: 262.

Vijayagopalan, K. (1971). Factice from rubber seed oil. *Rubber Board Bulletin*, **11**(2): 48-51.

Vijayagopalan, K. and Gopalakrishnan, K. S. (1971). Epoxidation of rubber seed oil. *Rubber Board Bulletin*, **11**(2): 52-54.