

DEVELOPMENT OF SURFACE COATINGS USING POLYESTER RESIN FROM CASHEW NUT SHELL LIQUID DERIVATIVES

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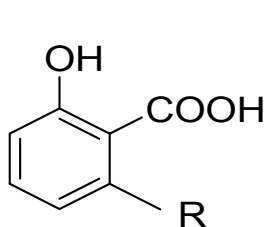
Abstract

Cashew Nut Shell Liquid (CNSL) is a by-product of the cashew nut industry waste. CNSL contains several phenolic compounds such as cardol, anacardic acid, cardanol, and methyl cardol. It is a dark reddish brown liquid and is an excellent source of natural resin. This research aims at developing surface coatings based on synthesized polyester resin from cardol, a derivative of CNSL. Polymerization of cardol with maleic anhydride was done under acidic conditions to formulate a polyester resin, which was dissolved in ethyl acetate solvent to develop surface coatings. The developed coating was found to have moisture content of less than 1%, viscosity (194.96 mm²/s), color (brown), specific gravity (1.978), acid value (12.7 mg KOH/g), iodine value (233.43 mg iodine/100g). FTIR analysis showed the presence of O-H stretching of the phenol, C=C aromatic ring vibration and C=O stretch. Tests done on commercial coatings from Dura Coat and Crown Paints showed presence of a broad peak observed in the region above 3000cm⁻¹ and was attributed to O-H stretch in phenols. The acid value was 10.5 mg KOH/g and had an iodine value of 243 mg iodine/100g. The color and viscosity varied while the moisture content was less than 1%. The investigation showed that the developed coating was of superior quality and could be comparable to the commercial coatings in the market.

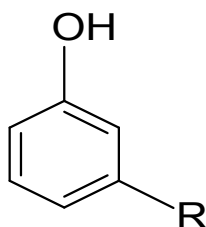
Key words: CNSL, Cardol, Polyester resin

1.0 Introduction

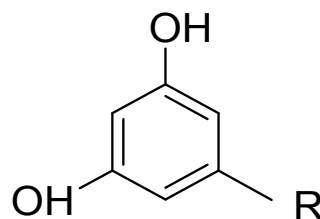
Cashew (*Anacardium occidentale* L.) nut shell liquid (CNSL) is a unique natural source for unsaturated long-chain phenols. Obtained as a byproduct of the cashew industry, this renewable material has wide applications in the form of brake linings, surface coatings, paints, and varnishes (Paramshivappa et al., 2001). The main applications of CNSL are in the polymer industry (Menon et al., 1985). Compared with conventional phenolic resins, CNSL polymer has improved flexibility (due to the internal plasticization effect of the long chain) and thus better processability. The side chain imparts a hydrophobic nature to the polymer, making it water repellent and resistant to weathering (Pillai et al., 1980). CNSL-based resins possess outstanding resistance to the softening action of mineral oils and high resistance to acids and alkalis (Knop et al., 1979). Based on the mode of extraction, CNSL is classified into two types, solvent-extracted CNSL and technical CNSL. A typical solvent-extracted CNSL contains anacardic acid (60-65%), cardol (15-20%), cardanol (10%), and traces of methyl cardol as shown in the figure below.



Anacardic acid (82%)



Cardanol (1.6%)



Cardol (13.8%)

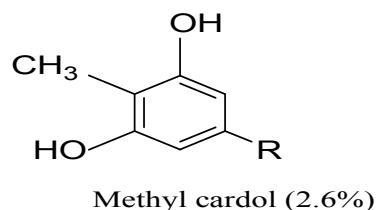


Figure 1: Chemical Components of CNSL

CNSL is obtained by roasting shells and contains mainly cardanol (60-65%), cardol (15-20%), polymeric material (10%), and traces of methyl cardol. Among the CNSL constituents, anacardic acid possesses antimicrobial, anti-acne, and many other medicinal properties (Grazzini *et al.*, 1991). Cardol, the dihydric component, accounts for CNSL's vesicant activity.

2.0 Materials and Methods

2.1 Extraction of Cashew Nut Shell Liquid

Batches of CNSL were extracted by solvent leaching method using n-Hexane. Solvent was employed in one batch of ground shells then shaken together to ensure the release of air and proper contact of solvent with shells. It was allowed to stand for 24 hours then the miscella transferred to the second batch. Each lot of miscella, after being passed through the cycle of extracting the three batches of the shells, was then allowed to stand for 24 hours to settle out the very fine particles of the ground shells contained in suspension, and the miscella was filtered through vacuum using a Buchner funnel, to separate it from the shells. The CNSL rich miscella was covered using aluminium foil to reduce loss of the solvent. The miscella was then put into a rotary evaporator to distill off the solvent at 65°C and condense it for re-use.

2.2 Decarboxylation of CNSL

The residual CNSL was heated to temperatures ranging from 135°C to 140°C for one hour until the frothing stops at the oil surface.

Figure 2: Decarboxylation of Anacardic Acid

2.3 Isolation of Cardol

Decarboxylated CNSL (100 g) was dissolved in methanol (320 ml), and ammonium hydroxide (25%, 200 ml) was added and stirred for 15 min. The methanolic ammonia solution was extracted with ethyl acetate/hexane (4:1) (1 _ 200 ml). The resulting organic layer was washed with 5% HCl (100 ml) followed by distilled water (100 ml), dried over anhydrous sodium sulfate, and concentrated to yield pure cardol (14g).

2.4 Synthesis of Polyester Resin

Polymerization of cardol with maleic anhydride was done under acidic conditions. One hundred grams of cardol was transferred into a clean 600ml beaker and heated in a water bath set at a temperature of 75°C. Thirty one (31g) of maleic anhydride was dissolved in 31cm³ ethyl acetate and added to cardol. One percent of the total weight of concentrated sulphuric was added drop by drop with continuous stirring and the reaction given 40 minutes to take place. The mixture was allowed to cool at room temperature.

2.5 Development of Surface Coating

Fifty grams of polyester resin was weighed in a 250 ml beaker and 25ml of ethyl acetate added then the contents were stirred using a magnetic stirrer to ensure even mixing after which the driers were added (i.e. 0.6g cobalt naphthenate and 1g of lead naphthenate respectively). Then 3g of anti-skin was also added while stirring. The formulations were left for an overnight, then applied on steel metal panels, glass panels and wood and allowed to dry in open air for 24 hours and curing time was recorded.

2.6 Adhesion Test

Cuts were made through the film to the substrate in one steady motion using sufficient pressure on the cutting tool to have the cutting edge reach the substrate. The film was then brushed lightly using a soft brush to remove any detached flakes of coatings. Additional number of cuts were made at 90o to and centered on the original cuts. The area was then cleaned with the brush as before. An unused strip of pressure sensitive tape was applied firmly across the surface of the test area removing all air entrapment. The time between application and removal of tape was one minute. The tape was removed by a rapid pull force applied approximately perpendicular (right angle) to the test area. The tape and test area were visually examined for evidence of any portion of the material tested having been removed from the specimen. Any evidence of material removed by the test was noted.

3.0 Results and Discussion

Table 1: Yield of raw CNSL and the amount of solvent recovered

Amount of ground cashew nut shell used (g)	200	600
Amount of raw CNSL obtained (g)	62.7	190.3
Average % yield (m/m)	30.9	178.9
Solvent used (g)	600	1800
Solvent recovered (g)	432	1314
Average % recovered solvent (m/m)	72	73

Table 2: Yield of cardanol obtained and the amount of solvent recovered

Amount of decarboxylated CNSL used (g)	30	100
Amount of cardol obtained (g)	3.9	13.4
Average % yield (m/m)	13.2	13.4
Solvent used (g)	60	200
Average % recovered solvent (m/m)	62	62

From Table 1 and 2 above, the percentage yield of CNSL obtained using the batch extraction method is high, this shows that there's maximum extraction using n-hexane. The yield of cardol isolated is also high implying that the chemical method of extraction is very efficient. The solvent recovered for extraction of CNSL and cardol is 60 % and above implying that a small amount of the solvent is lost to the environment.

Table 3: Characterization of raw CNSL, Decarboxylated CNSL and cardol

Parameter	Raw CNSL	Decarboxylated CNSL	Cardol
Specific gravity@ 25 °C, g/cm ³	0.99	0.96	0.95
Viscosity, cps	52.36	46.56	45.31
Acid value, g/100 g KOH	12.64	1.73	1.18
Iodine value, g/100 g	239.8	240.8	241.04
pH @25 °C	3.07	6.02	6.16
Moisture content	Negligible	Negligible	Negligible

There is a significant difference in the viscosity values of raw CNSL, decarboxylated CNSL and cardol (Table 3). Raw CNSL has anacardic acid as the major fraction with the $-\text{COOH}$ group in the ortho position of the phenol core and therefore there is strong dipole-dipole attraction between the partially positively charged hydrogen atom and the strong electronegative oxygen atom. There is the effect of intramolecular hydrogen bonding which results in the molecule being entangled together as it flows down the capillary tube as a result the shear rate increases and thus a high viscosity in CNSL as compared to decarboxylated CNSL and cardol. There is significant difference in the PH value of raw CNSL, decarboxylated CNSL and cardol as shown in Table 3. The Raw CNSL used is highly acidic with a pH of 3.07 as compared to decarboxylated CNSL PH 6.02 and cardol PH 6.16 indicating that the carboxylic acid content in the liquid is very high. Decarboxylated CNSL and Cardol are less acidic because heating CNSL decomposed the anacardic acid into cardanol and the carboxylic acid group was lost as a gas. There is no significance difference in the moisture content of raw CNSL, decarboxylated CNSL and cardol as shown in table 3. This is because during decarboxylation at 140°C water is lost.

Interpretation of Gas Chromatography/Mass Spectrometry (GC/MS) Fragmentation Processes

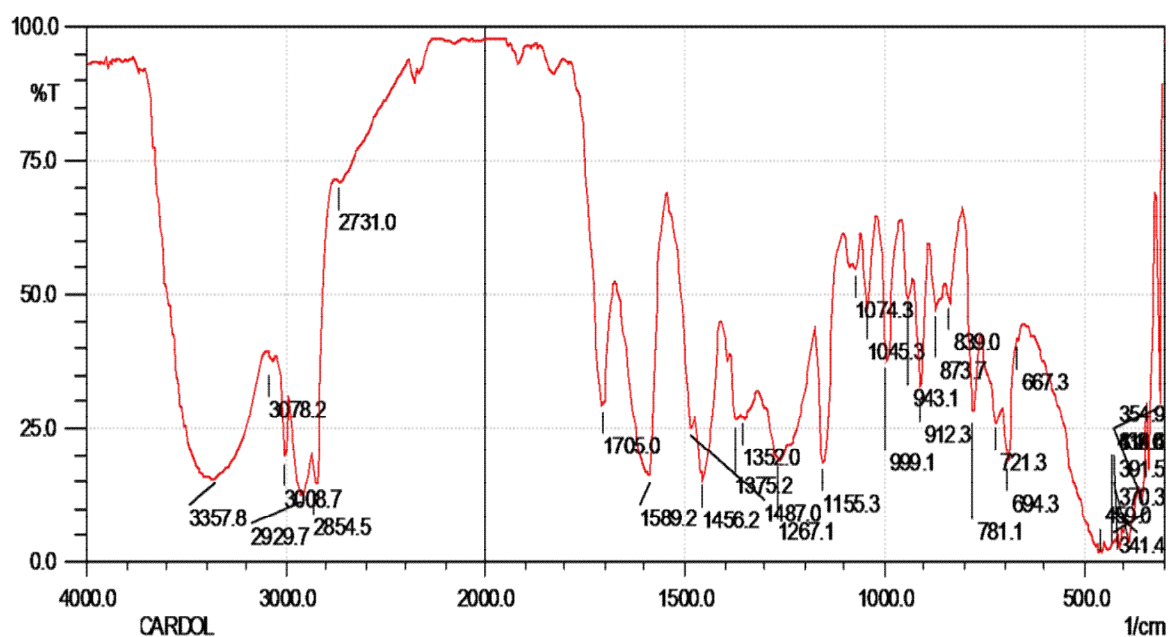


Figure 3: FTIR spectrum of cardol

The strong broad band at the region of 3350cm^{-1} shows the presence of O-H stretch group and the one at 3008cm^{-1} suggests the presence of C-H stretch mostly attached to a double bond or aromatic group. The peaks at 2925cm^{-1} and 2854cm^{-1} shows the presence of C-H stretch asymmetric and symmetric respectively, this is a characteristic C-H stretch which occurs at this region. The strong peaks at 1705cm^{-1} and 1589cm^{-1} suggests presence of carbonyl and C-C stretch of aromatic ring respectively due to 3008cm^{-1} C-H stretch at a higher region. The region 1155cm^{-1} to 999cm^{-1} suggests presence of heavy aromatic compounds because of multiple peaks which signify the C-H in plane bending vibration. Multiple strong peaks between 850cm^{-1} to 670cm^{-1} also indicate the presence of aromatic ring and peaks attributed to C-H out of plane bending vibration.

Interpretation of Gas Chromatography/Mass Spectrometry (GC/MS) Fragmentation Processes

A fragmentation process that is used to evaluate and predict ion fragments is the McLafferty rearrangement. In the McLafferty rearrangement a radical center in the molecular ion derived from a lone pair or a pi bond, abstracts a hydrogen from the gamma (γ) position, a pi bond is formed between the β and γ positions, and the bond between the α and β positions is broken.

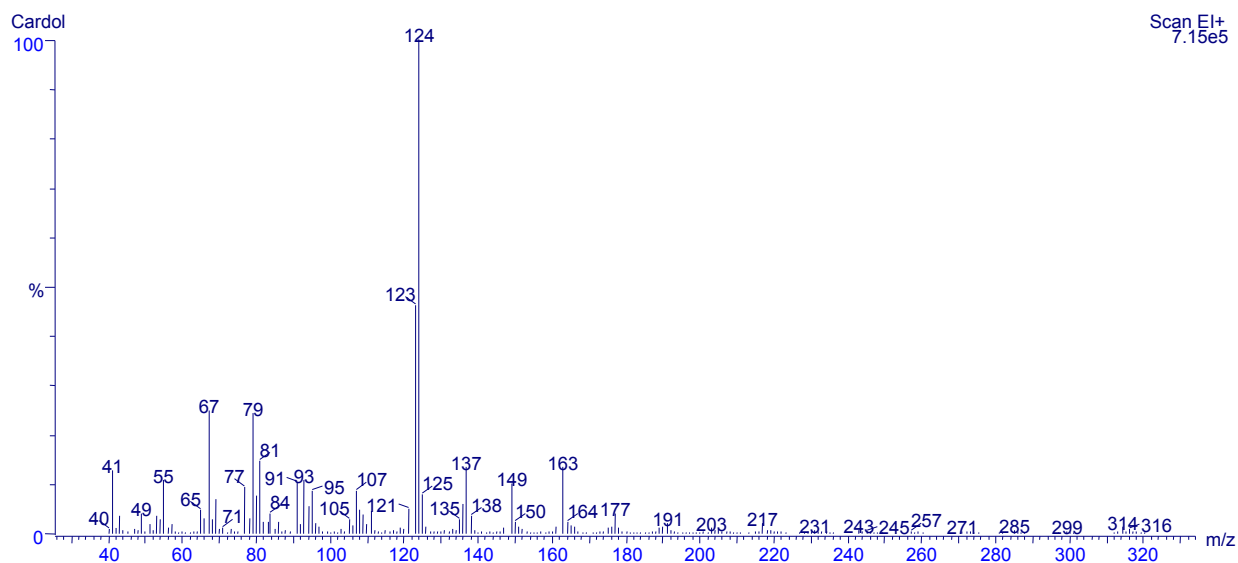


Figure 4: GC-MS profile of cardol

Cardol was analyzed by GC-MS with selective ion monitoring (SIM) figure 4. The main fragmentation ions of cardol are those at m/z 124 due to McLafferty rearrangement, m/z 123 due to β cleavage and m/z 137 due to γ cleavage. The identity of cardol was confirmed by the base peak at m/z 124.

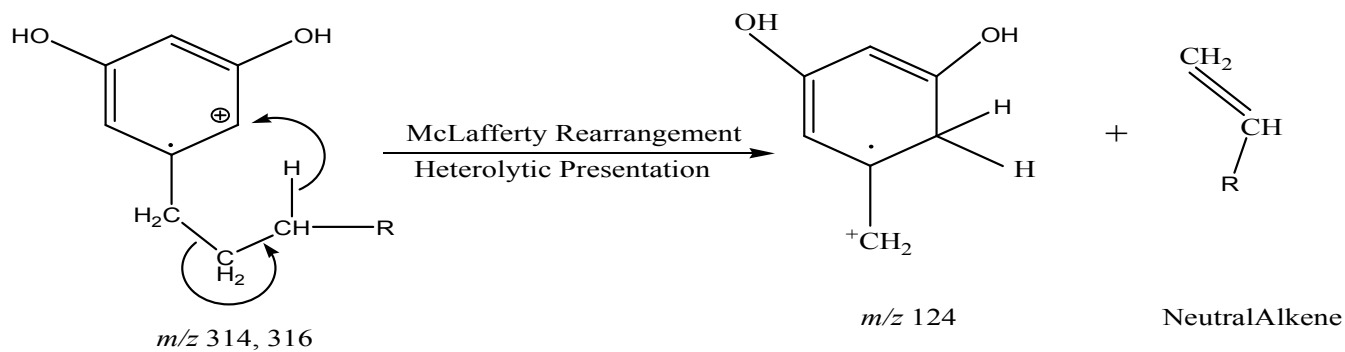


Figure 5: Heterolytic fragmentation of cardol

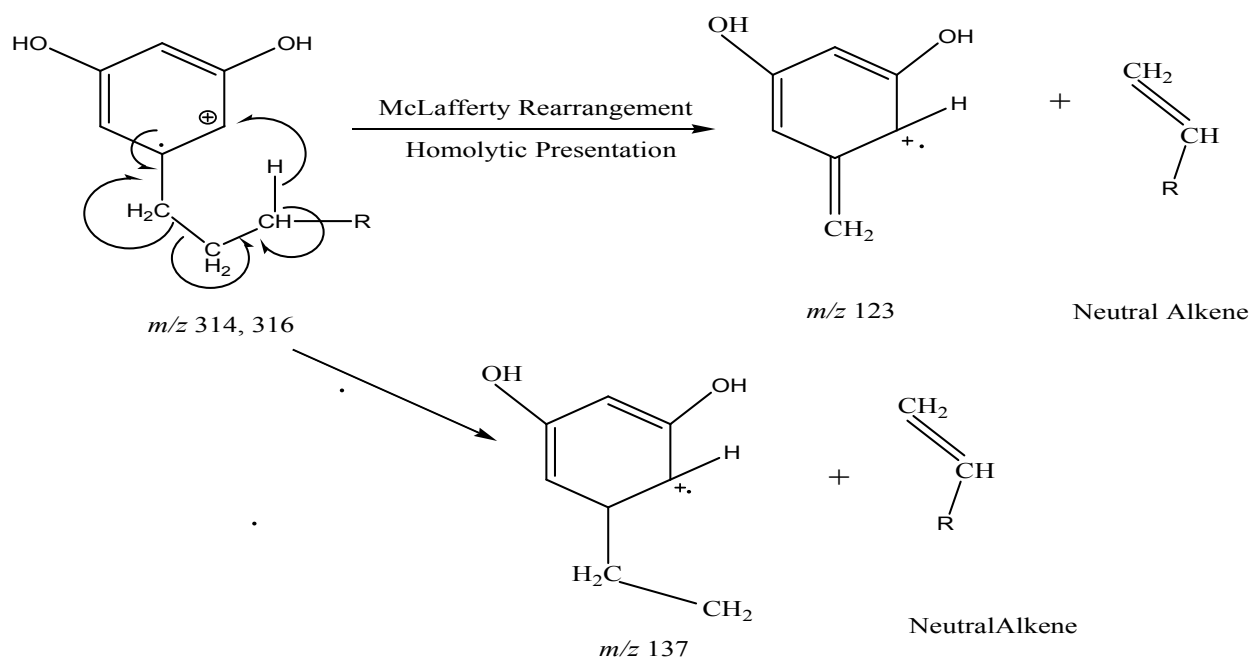


Figure 6: Homolytic fragmentation of cardol

Table 4: Characterization of commercial and developed coatings

Parameter	Dura Coat	Crown Paints	Developed Coating
Acid Value(mmKOH/g)	10.1	10.6	12.7
Viscosity(mm ² /s)	187.65	189.46	194.96
Iodine Value(mgl/100g)	243.34	243.58	233.43
Specific Gravity(g/cm ³)	1.94	1.89	1.978
Volatile Matter(%)	Less than 1%	Less than 1%	Less than 1%

There is a significant difference in the acid values of commercial coatings and the developed coatings. Acid value is a measure of free fatty acids in a given oil, this shows that there is a lot of free acids in all the coatings. There is no significance difference in the iodine values of commercial coatings and the developed coatings as shown in Table 4. This is because iodine value is a measure of the amount of unsaturation in given oil like the unsaturation in cardol. The high iodine values of more than 140 in the fractions show that they are drying oils. In all the coatings the volatile matter was very little and this implies very small amounts of solvents evaporate to the atmosphere.

Table 5: ASTM Classification for Adhesion Test

Classification	% of area removed	Remarks	Ratings
5B	None 0	Excellent	5
4B	Less than 5%	Very Good	4
3B	5 – 15%	Good	3
2B	15 – 35%	Fair	2
1B	35 – 65%	Poor	1
0B	Greater than 65%	Very Poor	0

The adhesion performance of the developed coating was rated as good as compared to the commercial ones which was rated excellent. The figure below compares the results of adhesion.

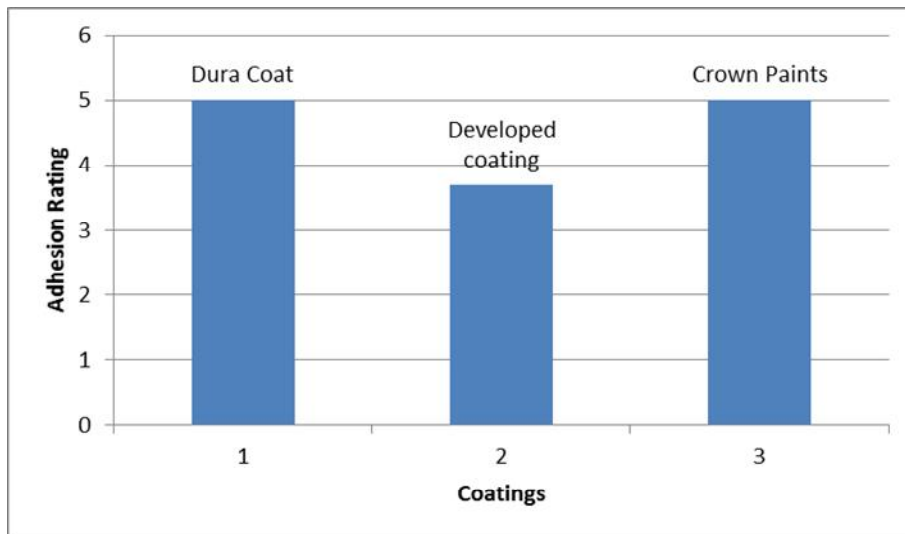


Figure 7: Comparison of adhesion in coatings

4.0 Conclusion

From the findings it was established that the developed coating had comparable characteristics to the commercial coatings.

Acknowledgements

We acknowledge Jomo Kenyatta University of Agriculture and Technology through Research Production and Extension for financial support.

References

Grazzini, R., Hesk, D., Heininger, E., Hildenbrandt, G., Reddy, C. C., Cox-Foster, D., Medferd, J., Craig, R., Mumma, R. O. (1991). Inhibition of lipoxygenase and prostaglandin endoperoxidase synthase by anacardic acids. *Biochem. Biophys. Res. Commun.* **176**, PP 775-780.

Knop, W., Scheib, A. (1979). *Chemistry and Applications of Phenolic Resin-Polymer Properties and Applications*; Springer Verlag: Berlin, Germany.

Menon, A. R. R., Pillai, C. K. S., Sudha, J. D. and Mathew, A. G. (1985). Cashew nut shell liquids Its polymeric and other industrial products. *J. Sci. Ind. Res.*, **44**, pp 324-338.

Paramshivappa, R., Phani Kumar, P., Vithayathil, P. J. and Srinivasa Rao, A. (2001). Novel method for isolation of major phenolic components from cashew (*Anacardium occidentale* L.) nut shell liquid. *J. Agric. Food Chem.*, **49**, 2548-2551.

Pillai, C. K. S., Prasad, S. V., Rohtagi, P. K. (1980). To Evaluate the Polymerisation Characteristics of Cashew Nut Shell Liquid Obtained from the Expeller; Report RRL/M/27/29; Materials Division, Regional Research Laboratory: Trivandrum, India.