MODIFICATION OF GUMMY MASS WITH BIOMINE RESIN: AN INDUSTRIAL WASTE AS A SOURCE OF INCOME

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ABSTRACT

Gummy mass (GM) is filtered out as industrial waste in manufacturing of Aleuritic acid in the form of effluent. It poses a problem for aleuritic acid manufacturers for its proper disposal as it is sticky material and does not dry at ambient temperature. GM was prepared from effluent of aleuritic acid collected from lac industry. Characterization of GM was carried out using Fourier Transform Infra Red (FTIR) and Differential Scanning Calorimetric (DSC) analyses. GM was modified with Biomine resin (a synthetic resin). Films of the modified products were baked at elevated temperature. FT-IR Spectroscopic and DSC analysis of air-dried and baked films of the modified products were carried out. FTIR spectra showed esterification reaction between carboxyl group of GM and hydroxyl group of the resin. DSC thermograms revealed more softening and broad peak in the air-dried film, whereas baked film of the modified product showed thermal stability at higher concentration of the resin. Coating properties and adhesive strength of air-dried and baked films of the modified products were studied. Adhesive strength, scratch hardness and impact resistance were found to be higher where GM percentage was higher. Adhesive strength of baked films was higher than air dried films while impact resistance was found better for air-dried films than baked films. Gloss increased with the increase in concentration of the resin while scratch hardness was adversely affected. Films of the modified products were found to be flexible. Baking of the films improved gloss and scratch hardness property of the modified products. Based on the study, it is concluded that the GM modified with the resin may be utilized in preparation of varnishes (metal lacquer, insulating varnish etc.) and paints. This will lead to a secondary source of income to aleuritic acid manufacturers and also others.

Keywords: Gummy mass, Aleuritic acid, Effluent, Coating material, Biomine resin

Introduction

Gummy mass (GM) is an industrial waste, filtered out as effluent in manufacturing of Aleuritic acid. Aleuritic acid is the main acid constituent of lac, which is present in the lac resin to the extent of 35-43%. But, generally, 18-20% of aleuritic acid is extracted from lac in the laboratory. In industry, maximum up to 13-14% of aleuritic acid is produced from lac. Rest is filtered out in the form of effluent (GM) which is about 80-85% of lac resin. GM is often a problem for aleuritic acid manufacturers for its proper disposal, as it is very sticky in nature. India is the leader in aleuritic acid production and almost 100% of aleuritic acid is exported to different countries. Exporting around 162t of aleuritic acid (2013-14), country earned revenue of ₹10, 054.42 lakh. Quantity of gummy mass production can be calculated to be more than 900t per year.

Gummy mass is sticky material and does not dry at its own, at ambient temperature. It consists of sesquiterpenic acids and a small fraction of aliphatic acid. In the past, efforts were made to formulate gummy mass based cementing composition for automobiles (Agarwal and Srivastava, 1986). The by-product has been utilized in formulation of high thermal resistant insulating varnish, in preparation of fibre-glass reinforced sheets (Goswami, *et al.*, 2004) and making particle board as a binder adhesive (Sao and Pandey, 2009).

Biomine resin is melamine formaldehyde (MF) resin. It is an amino resin, is a condensed product of melamine and formaldehyde. MF resins are never used alone as they form very hard and brittle films. However, they offer very good and varied properties when used along with other resins (Chattopadhyay, et al. 2003a, Chattopadhyay, 2003b). Kumar (1965) developed a varnish formulation based on shellac-MF resin. MF resin has been tried for modification of lac by other research workers (Majee and Kumar, 1970 & Bhatia *et al.* 2006). They have concluded that blending of lac with MF resin resulted in a varnish which gave hard, smooth and glossy films. The varnish was very resistant to water, beverages and liquors as no blushing or spoilage was observed on contact with them. Recently Ansari *et al.* (2012) improved coating properties of shellac-rosin blends by treatment with MF resin.

Aleuritic acid manufacturers often demand for utilization of GM, as it poses a great problem for its disposal. Therefore, in the present study , attempts have been made to create avenues for its utilization. Besides, Aleuritic acid manufacturers will be benefited further with the use of gummy mass in the form of additional income.

Materials and Methods

Gummy mass was prepared from effluent of Aleuritic acid, collected from lac factory M/s *Chem*shel Purulia (West Bengal). The effluent was acidified with 20% sulphuric acid, washed with water a number of times to free the acid and dried the precipitate completely to remove moisture. Yield of the GM was found to be 18-20% to the weight of the effluent. Biomine resin (1651, 60% solid content) was purchased from M/s Hard Castle & Waud Manufacturing Co. Ltd, Mumbai. Ethyl alcohol purchased from local market was used after distillation. Butanol and toluene were used of M/s Merck Chemicals.

Acid and saponification values of the GM were determined out using standard procedure and compared with those of lac. FT-IR study was carried out, with IR-Prestige 21 instrument by Shimadzu Corporation, Japan. Differential Scanning Calorimetric (DSC) analysis of GM was carried out using TA DSC 20-Q analyzer.

GM was modified with Biomine resin in liquid medium. 20% solution of shellac in ethanol was reacted with 20% solution of Biomine resin in butanol in certain proportions to make it 7:3, 1:1 and 3:7 (v/v). Parent Solutions of shellac and Biomine resin were kept as control. Physicochemical properties of modified products such as acid value, saponification value, specific gravity, viscosity and bleach index were carried using standard procedure. Films were developed on pre-cleaned and degreased tin panels and glass slides by flowing method. Brush was applied for coating on prepared wooden panels. Baking of the films was done on coated tin panels at 150±5^{O}C in air oven for 20 minutes. Properties of the modified products were studied using standard procedure. Gloss of the films was measured on tin panels as well as on French polished wooden panels at an angle of 45^{O} according to ASTM: D 523-99. Gloss was recorded comparative in respect of standard black stone

(57%). Flexibility of films developed on tin panels was measured as per ASTM D522, with conical mandrel by rotation of the roller frame, tapers from 37mm to 3mm diameter. Scratch hardness was measured by an automatic scratch hardness tester as per British Standards Method of test for Paints (BS3900: Part E2). Impact resistance of the cured film samples on tin panels was conducted as per BS 3900 (Part E3) by dropping a hemi-spherical shaped indenting tool (diameter 7mm) weighing 10.5 lb from a height of 22.5 inch over the panels. Water resistance was carried out according to ASTM D 5402. Heat resistance of the cured films was determined on coated wooden panels by putting the 600ml beaker containing boiling water for 2 minutes (6).

Results and Discussion

Preparation and characterization of Gummy Mass

The GM prepared was characterized. Acid value and saponification value of the GM were found in the range of 162-181 and 180-193 respectively. Acid value and Saponification value of GM was found to be higher as compared to shellac indicating the free carboxyl groups present in the GM (Figure 1).

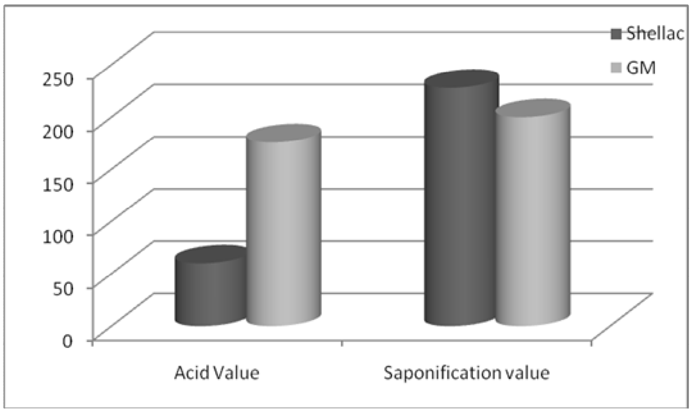

Figure 1. Acid value and saponification value of shellac and GM

FTIR study

Comparative FTIR spectra of GM and lac have been depicted in the figure 2. From the spectra, it is evident that intensity and sharpness of carbonyl group and $-CH_3$ and $-CH_2$-frequency increased in GM as compared to lac indicating the free caboxyl groups and –CH moiety present in GM.

DSC analysis

Figure 3 shows DSC thermograms of Gm as well as shellac. The thermogram of GM showed no peaks but fluidity while shellac shows peak at 63^{o}C (Figure 3). Glass transition temperature (Tg) of GM was found to be -15.67 ^{o}C which is very much low as compared to shellac (-11.56 ^{o}C).

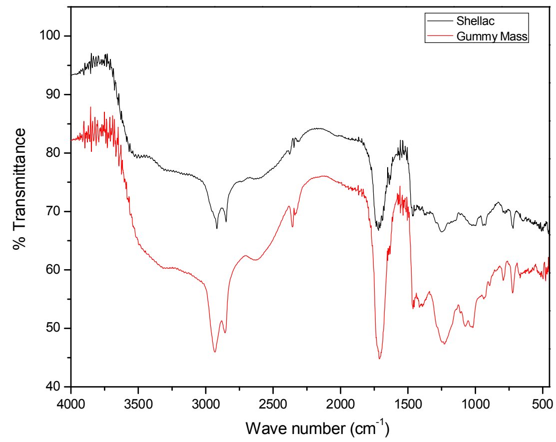

Figure 2 FTIR spectra of shellac and GM

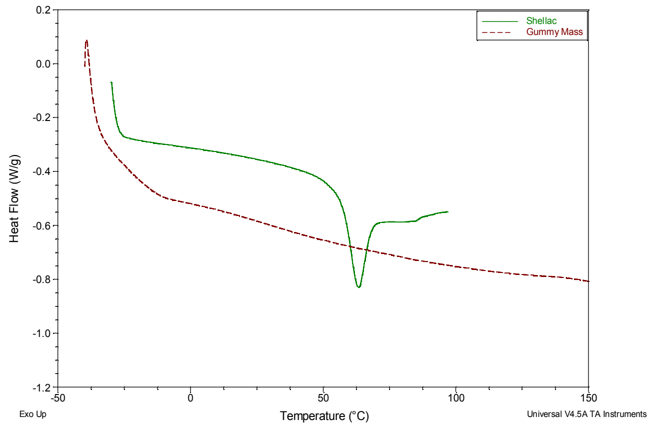

Figure 3: DSC thermograms of shellac and GM

Modification of Gummy Mass with Biomine resin

GM was modified with Biomine resin (BM) and properties of air-dried and baked films of the modified products were studied. Films developed on cleaned steel panels were dry, smooth and very glossy in nature. Gloss increased with the increase in concentration of amino resin. Baking further improved gloss of the films (Figure 4). GM modified with BM was developed in to powder form. The modified product was soluble in alcohol but insoluble in hydrocarbon solvents. Specific gravity of 25% solutions of modified products was found in the range of 0.88-0.89g/ml. Viscosity of 30% solutions of the modified products was measured to be 30-32 cP and 14 seconds by B4 Flow cup. Acid value of the modified products decreased (80.34) and further decreased with the increase in concentration of Biomine resin. Saponification value of the modified products decreased (182) but increased with the increase in concentration of Biomine resin. Bleach index of the modified GM was recorded 162. Adhesive strength and impact resistance were found to be higher where GM % was higher. Adhesive strength decreased with the increase in ratio of MF resin. Baking improved the adhesion of the films (Figure 5). Scratch hardness increased on increasing the concentration of the resin up to (1:1) and then decreased. Baking improved scratch resistance property (Figure 6). Impact resistance was higher for air-dried films than baked films. Baking increased the brittleness in the films, losing the adhesion of the films on impact of the block. Flexibility test was passed by all the compositions of GM.

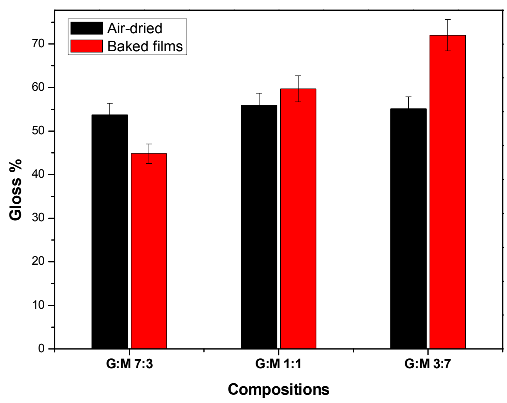

Figure 4: Gloss of Air-dried and baked films of G

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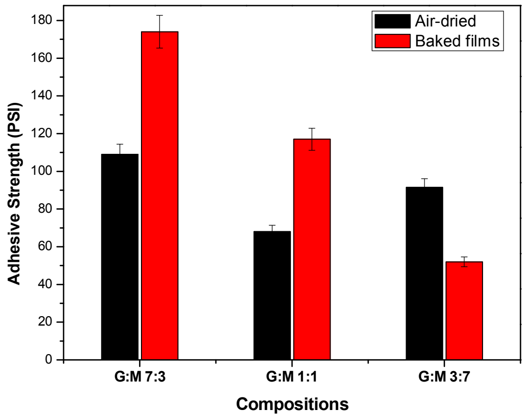

Figure 5: Adhesive strength of Air-dried and baked films of GM modified with MF resin

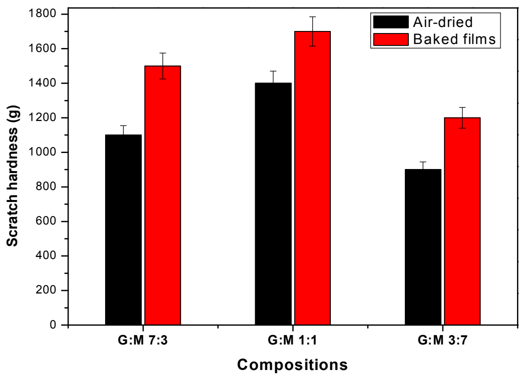

Figure 6: Scratch resistance of Air-dried and baked films of GM modified with MF resin

FT-IR Spectroscopy

FT-IR Spectroscopic analysis of air-dried and baked films of GM and GM modified with BM resin was carried out. The peak frequency of carbonyl group of GM shifts to lower wavelength (Blue Shift) and intensity of the peak decreased on reaction with BM which further decreased on increasing the concentration of the BM resin. The peaks intensity for -CH3 and –CH2— moiety decreased which increased on increasing the concentration of the BM resin. N-H stretching vibration frequency prominently appeared at 3335 cm^{-1} on increasing the concentration of BM resin (Figure 7).

On baking the films, intensity of –CH3 and –CH2- moiety increased which decreased on increasing the concentration of BM resin. More broad peaks for –NH asymmetric stretching vibrations was observed. Sharp and prominent peaks at 813 cm^{-1} appeared for out of plane deformation vibrations of triazine ring of BM resin. The sharpness and intensity of the peaks increased on increasing the concentration of BM resin. The analysis indicated the esterification reaction between carboxyl group of GM and hydroxyl group of the BM resin (Figure 8).

Thermal behaviour

Air-dried films of GM modified with BM resin have been shown in the Figure 9. It was observed that after modification with the resin, Decrease in softening of GM was observed and little softening in the films was observed between 40-100^{o}C and a broad peak was observed around 165 ^{o}C. GM showed thermal stability after modification with the resin to some extent but as the concentration of the resin was increased, more softening of the films was observed more prominent peak at 170-175 ^{o}C was observed. Whereas baked films of the modified products showed reverse order (Figure 10). GM modified with BM resin (7:3) showed prominent softening point at 74 ^{o}C, which reduced on increasing the concentration of BM resin and very little softening was recorded in GM:BM (3:7) ratio indicating the thermal stability at higher concentration of BM resin. Comparing air-dried and baked films of GM modified with BM resin, more softening and broad peak was found in the air-dried film, in the composition where higher concentration of BM resin was there whereas baked film of the modified product showed more thermal stability at higher concentration of BM resin (Figure 11).

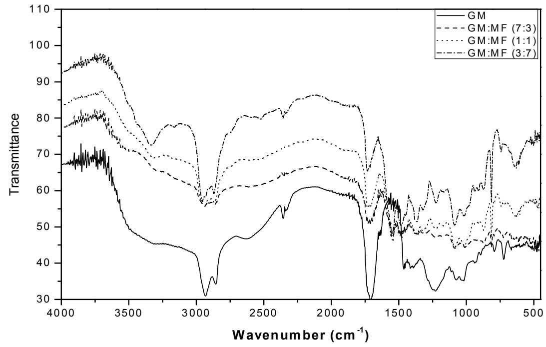

Figure 7: FTIR spectra of air-dried films of GM modified with BM resin

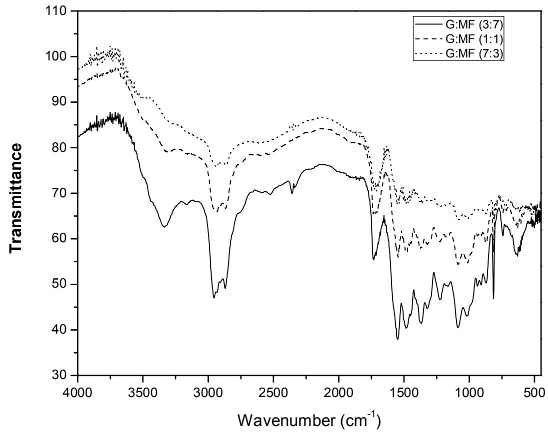

Figure 8: FTIR spectra of baked films of GM modified with BM resin

Thermo-gravimetric analysis (TGA) of the GM modified with Biomine resin were carried out. TGA thermograms of GM modified with BM resin also exhibited thermal stability up to 200 ^{0}C and then degradation started. Complete degradation was recorded around 550 ^{0}C (Figure 12).

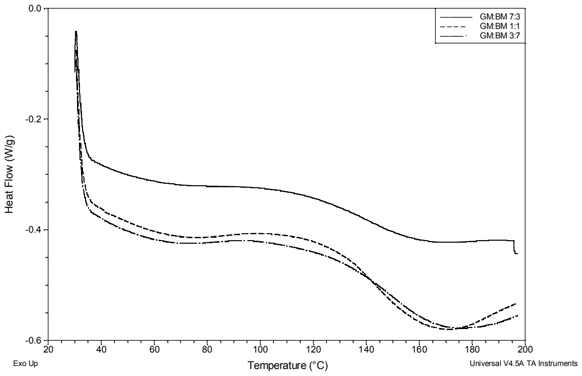

Figure 9: DSC thermograms of air-dried films of GM modified with BM resin

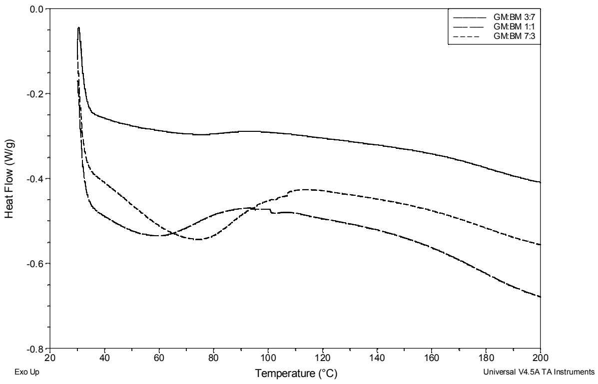

Figure 10: DSC thermograms of baked films of GM modified with BM resin

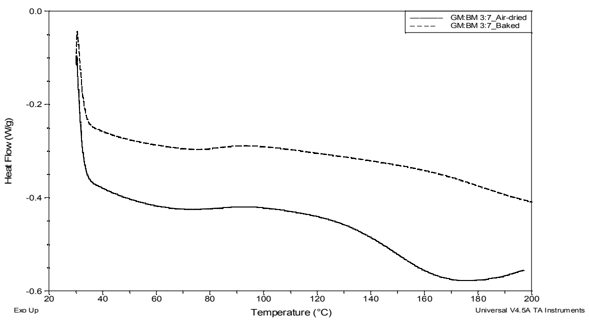

Figure 11: Comparative DSC thermograms of air-dried and baked films of GM modified with BM resin (3:7)

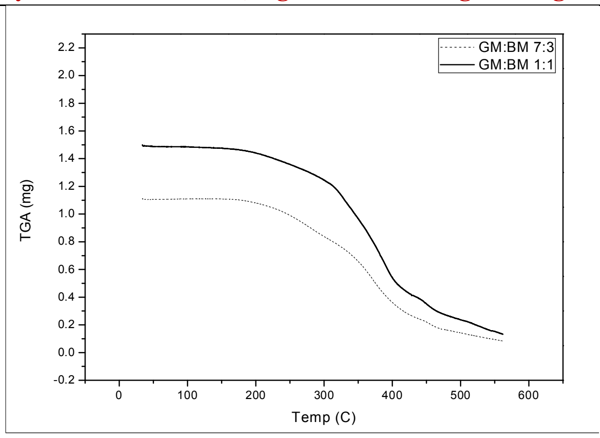

Figure 12: TGA thermograms of GM modified with BM resin

Road marking paint and enamel paint

Gummy mass modified with BM resin were utilized in preparation of enamel paint and road marking paint. Formulations of enamel paint were prepared and their properties such as drying time, viscosity, fineness of grind gauge, finish, gloss, scratch hardness, solid content, and water resistance were evaluated as per BIS specifications. Gloss and scratch hardness of the paint formulations are given in Figures 13 & 14. The paints showed fairly good performance. Formulations of road marking paint were prepared and applied on the Institute road for their evaluation. One of the formulations showed some encouraging results but did not find its suitability as road marking paint. The modified products were also used in preparation of insulating varnish. Properties of the varnish were evaluated and found satisfactory.

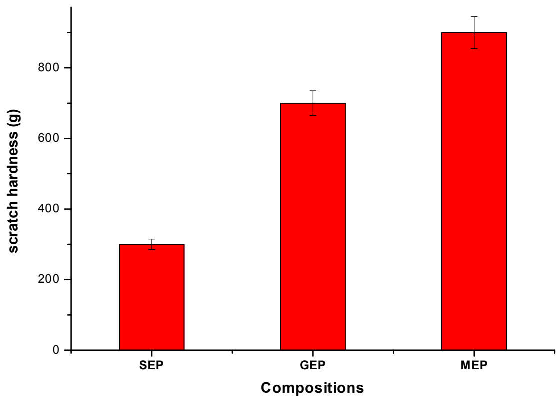

Figure 13: Gloss of enamel paints

Figure 14: Scratch hardness of enamel paints

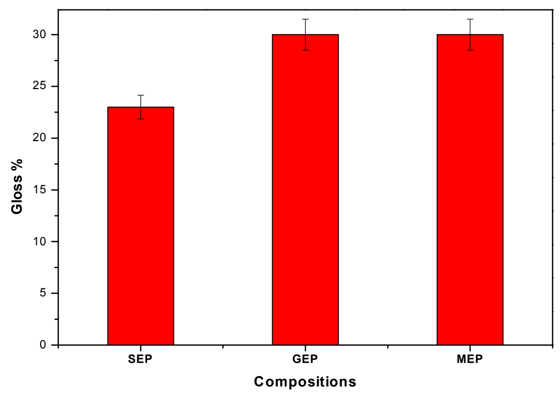

Figure 14: Scratch hardness of enamel paints

Conclusion

The study yielded that GM may be utilized in the development of metal lacquer, insulating varnish, gasket shellac cement compound for automobile industry, enamel paint for metal surfaces, adhesive for tackifier and a number of other areas of applications. The development will lead to not only solve the problem of aleuritic acid manufacturers, but a source of income to manufacturers.

References

Agarwal, S C and Srivastava, B C (1986). Gummy mass based cementing composition for automobiles, *Res. Ind*. **31**(3): 244.

Ansari, M F, Sarkhel, G, Goswami, D N and Baboo, B, (2012). Effect of butylated melamine formaldehyde resin on coating properties of shellac-rosin blends, *Asia Pacific Coatings Journal*, **25**(5): 35-38.

Bhatia, D, Sarkar, P C and Alam, M, (2006). Specular Reflectance and Derivative Spectrometric Studies on Lac-Melamine Formaldehyde (MF) Resin Blends, *Pigment & Resin Technology*, **35**(5): 260-9.

Chattopadhyay, D K, Chakravarti, B K, Narayan, R and Raju, K V S N (2003a). Properties of Acrylic Melamine Coatings based on High Conversion Prepolymer, *Paintindia*, **53**(7): 45-56.

Chattopadhyay, D K, Rohini, D B K and Raju, K V S N, (2003b). Effect of Polymerization Techniques on the Properties of Acrylic-Melamine Coatings, *Paintindia*, **53**(7): 47-56.

Goswami, D N, Prasad, N, Jha P C and Mahto, K (2004). Utilization of gummy mass: a by-product of lac industry, *Indian Journal of Chemical Technology*, **11**, January: 121-26.

Kumar, S, (1965). A Heat and Water Proof Shellac Finish for Wood, *Paint Technology*, **30**(2): 16-22.

Majee, R N and Kumar, S, (1970). A Sprayable Heat, Water and Liquour Proof Shellac Varnish for Wooden Furniture, *Res. Ind.,* **15:** 192-94.

Sao, K P and Pandey, S K (2009). Utilization of aleuritic free gummy mass: an industrial by-product for making particle board, *Journal of Chemical Technology*, Vol. **16**, March: 192-95.