

## Shellac-a potential raw material for polyurethanes

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URETHANE Polymers were discovered by Bayer and co-workers<sup>1</sup> in 1937. They investigated these Polymers for commercial use and during the Second World War foamed products, coatings, adhesives and even an elastomer were developed and gradually came into industrial use. Since then the technology and economic importance of Polyurethanes have developed at a very rapid rate. Polyurethanes now find wide applications in flexible and rigid foams, coatings, adhesives, plastics and elastomers. They possess excellent resistance to alkalis, acids, oils and most of the solvents and chemicals. They also possess very good adhesion to metals, wood, fibres, glass and ceramics. Polyurethane foams are known for their high strength with light weight, excellent thermal insulation and good heat resistance.

These are generally prepared by reaction of Polyisocyanates with polyhydroxy compounds such as polyethers, polyesters, castor oil or glycols. Compounds containing groups such as amino and carboxyl may also be used. Thus polyurethanes do not actually contain primary urethane groups, but are those polymers which contain significant number of urethane groups regardless of what the rest of molecule may be. A typical polyurethane may contain in addition to urethane groups, aliphatic and aromatic hydrocarbon residues esters, ethers, amide and urea groups. Polyurethanes are sometimes called simply 'urethanes'.

Shellac, a well known natural resin behaves more like a polyester as it is consisted of inter- and intra-esters of polyhydroxy carboxylic acids with about five hydroxyl and one carboxyl groups free in an average molecule (Mol. Wt. 1000). Thus it should be possible to react shellac with polyisocyanates to form polyurethanes. From the practical point of view it may not be very convenient to use shellac as it is, particularly for coating compositions as its solubility in common non-hydroxy solvents is poor. But presence of many reactive groups in shellac provide ample scope for its modifications to obtain products with desired properties. For example, shellac can easily be combined with drying or semi-drying oils in presence of certain incorporating agents. Oil modified shellacs are soluble in non-hydroxy solvents such as, esters, ketons and hydrocarbons. Shellac can also be reacted with glycols, fatty acids, urea and many other such chemi-

cals and it is possible to get products with desired reactivity. Apart from these, shellac is a good film forming material, it has good adhesion to a variety of surfaces and a good insulator of electricity. It has lost ground in many industries mainly due to its brittleness, low softening point and poor resistance to solvents and chemicals. But with all the above mentioned properties it has much potentiality as raw material in many industries.

Recently some interesting urethane compositions based on shellac/modified shellac have been reported in the literature. These are summarised below :-

A stable one pack coating compositions prepared from 'blocked' isocyanates and dry shellac has been described in an American patent<sup>2</sup>. The diisocyanate is blocked with cyclohexanol or phenol and then added to a shellac solution prepared by dissolving shellac in dry methyl ethyl ketone at 56°C. The resulting coating composition is cured by even heating at 120°C.

In another<sup>3</sup> claims have been made of stable coating compositions prepared from dry shellac and organic diisocyanate which can be applied to a substrate and require no heat curing. Shellac is dissolved methyl ethyl ketone, cyclohexanone or their mixture at 75°C and toluene diisocyanate added at controlled temperature. If less than stoichiometric ratio of isocyanate is added the product is a modified shellac with improved properties. If the isocyanate/shellac stoichiometric ratio is greater than one the product is cured not only by inter action but also by reacting with moisture in the air. These products have been reported to possess greater toughness, reduced water sensitivity, excellent abrasion resistance, durability to exposure and resistance to chemicals and many solvents. These compositions are claimed to be useful for coating leather, mirror backing stiffening or water proofing agents and in treating textiles and papers to improve their water resistance and repellancy.

A coating composition based on castor oil modified shellac<sup>4</sup> and toluene diisocyanate has been reported to possess excellent properties in respect of scratch hardness, flexibility, gloss and resistance to solvents and chemicals. A shellac linseed oil/glycerol combination<sup>5</sup> has also been reported to be an excellent vehicle for urethane coating system. The

alcoholysis products of linseed oil with glycerol are combined with 30-60% of shellac. The resulting product is diluted with white spirit and mixed with toluene diisocyanate at the time of use. The resulting coating composition produces films which cure at ordinary temperature and possess excellent gloss, hardness and flexibility. They are also resistant to solvents and chemicals. Shellac modified with the alcoholysis products of linseed oil and propylene

glycol<sup>6</sup> has also been reported to make a good vehicle for urethane coating system.

Very recently the use of shellac for preparation of rigid polyurethane foams has been reported. Shellac is reacted with glycol or glycol-dibasic acid mixture to obtain shellac based polyesters. These are then converted into rigid polyurethane foams by reacting with polyisocyanate under suitable conditions. Rigid polyurethane foams obtained from shellac based polyesters has been claimed to possess properties comparable to those of imported polyurethane foams used for making artificial limbs.

Shellac has been losing ground in many fields due to tough competition from synthetic. Its survival depended mainly on its diverse uses. Its possible utility as a raw material for urethane coatings and foams may bring a new opening for shellac.

### Polyurethane reactions

1.  $R_1HO + NCO \rightarrow R_2NH - COOR_1$  (Urethane)
2.  $HO-R-OH + OCN-R^1-NCO \rightarrow$   

$$\sim (R-O-\overset{\overset{O}{\parallel}}{C}-NH-R^1-NH-\overset{\overset{O}{\parallel}}{C}-O) \sim$$
 (Polyurethane)
3.  $RNCO + R^1NH_2 \rightarrow RNH-\overset{\overset{O}{\parallel}}{C}-NHR^1$  Urea
4.  $RNCO + R^1COOH \rightarrow (RNH-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R^1) \rightarrow$   
 $RNHCOR + CO_2$   
 (amide)
5.  $Ar-NCO + R^1COOH (Ar-NH-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R^1) \rightarrow$   
 $(Ar-NH-\overset{\overset{O}{\parallel}}{C}-O-C-NH-Ar) + R^1-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R^1$   
 $(Ar-NH-\overset{\overset{O}{\parallel}}{C}-O-C-NH-Ar) \rightarrow Ar-NH-\overset{\overset{O}{\parallel}}{C}-$   
 $NH-Ar + CO_2$  Urea  
 (Urea)
6.  $RNCO + H_2O \rightarrow RNH-COOH \rightarrow RNH_2 + CO_2$

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