

Reprinted from the *Journal of Scientific & Industrial Research*, Vol. 35, August 1976, pages 538-542

## Polyurethane Aqueous Systems

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THE recent past has witnessed a sudden spurt of interest in the use of water-based coating systems, chiefly for ecological reasons. Today, more than ever before, pollution of environment has assumed alarming proportions and the awareness about this has prompted many industrially advanced nations like USA, Germany, etc., to enforce laws governing pollution control. A large volume of literature has accumulated on pollution and its control<sup>1-10</sup>. The type of pollution that results from the use of solvent-based coatings is mainly that of air. The pollution of air by solvents from coatings not only makes the surroundings uncomfortable for the worker, but also creates fire hazard. It has been estimated that 8-10% of smog formation in the atmosphere is due to solvent emissions from coatings<sup>11</sup>. These limitations of solvent-based coating systems have focussed attention on the development of alternative systems like aqueous systems, powder coatings, etc. Of these, water-based systems, apart

from offering advantages like non-pollution and freedom from fire hazard, are rapid drying and economical. They also enable rapid cleaning up of equipment. The wide acceptance of the aqueous systems by the industry is borne out by the dwindling usage of the solvent-based products from 164 m gal in 1966 to 37 m gal in 1975 and the increase in the usage of aqueous systems from 187 m gal in 1966 to 338 m gal in 1975<sup>12\*</sup>.

### Emulsion Polymerization and Its Applicability to Polyurethanes

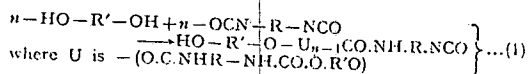
The obvious method of making aqueous dispersions of polymers is by carrying out the polymerization itself in the aqueous medium. If either the monomer(s) or the polymer is water-insoluble, recourse is taken to the so-called emulsion polymerization. But this direct method is inapplicable to the

\*These figures include both interior and exterior systems.

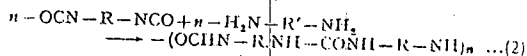
synthesis of polyurethanes for the simple reason that diisocyanates, one of the monomers used in this synthesis, are water-sensitive. No less easy is the replacement of solvent after the synthesis of polyurethanes by the solution method. The easiest way to overcome this difficulty is the provision of hydrophilicity in the urethane structure itself, without compromising on the other properties for which urethanes are very well noted. This implies the incorporation of the minimum number of hydrophilic groups in the polymer structure or subsequently destroying or rendering ineffective all such groups. The ways in which these could be achieved are briefly reviewed in this article.

### Methods of Making Non-ionic Aqueous Systems

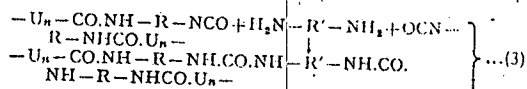
Polyurethanes are characterized by the presence of the group  $\text{NH.CO.O.}$  in their backbone. The structure of their repeating unit is  $-\text{OC.NH.R.NH.CO.O.R}'-$  and it is proposed to be indicated as U in all reactions mentioned in this paper. As implied in this structure, polyurethanes can and in fact are prepared by reacting a diisocyanate with a diol (Reaction 1). Hence, polyurethanes can be made hydrophilic by choosing at least one of these reactants which is hydrophilic. Usually polyethylene glycol or epoxide is chosen for this purpose as the hydroxyl component<sup>13,14</sup>. But the hydrophilicity of these products is so great that they are useful as textile coatings or as thickeners<sup>15</sup>. Treatment of NCO-ended urethane prepolymers with epoxide, however, can yield the desired product<sup>16,17</sup>.



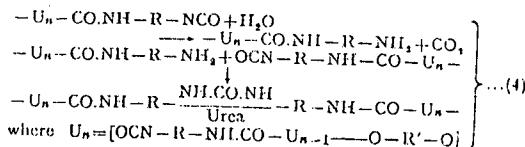
Non-ionic polyurethanes can also be produced by employing non-ionic emulsifiers<sup>18,19</sup>. The first attempt in this direction was made in 1943 by Schlack, the inventor of the caprolactum fibre. He reacted diisocyanates with diamines in the presence of non-ionic emulsifiers<sup>20</sup>, but could obtain only a polyurea and not a polyurethane (Reaction 2).



Later, the reaction was repeated with NCO-ended urethane prepolymers in place of simple diisocyanates. The products obtained were urethane-urea block polymers<sup>21-26</sup> (Reaction 3). These had two major defects. For one thing, reproducibility could not be achieved, as the process was diffusion controlled. And for the other, the products had only limited shelf-life. The bigger particle size due to the heterophasic nature of the reaction system was responsible for this. However, storage stability could be improved by high shear homogenization of the urethane prepolymer prior to reaction

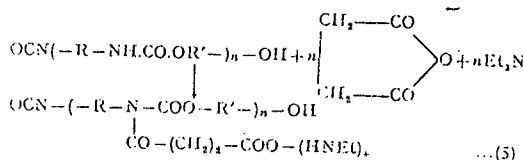


with diamine<sup>21</sup>. Urethane-urea polymer could also be obtained by allowing the NCO end groups of the urethane prepolymer emulsion to react slowly with the water medium itself<sup>22,23</sup> (Reaction 4). This second product, however, was inferior to the diamine-reacted one. Both still contained some solvent. They are useful as textile, leather and paper impregnants. To achieve satisfactory strength and water resistance, these systems require post-curing at elevated temperatures.



### Anionic Materials

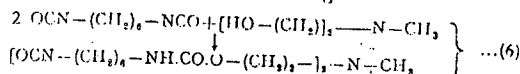
An excellent review on the preparation of the ionic polyurethanes was presented by Dieterich<sup>24</sup>. Of the two types possible, the anionic polyurethanes contain acid groups which can be neutralized by metallic or amine bases. They are often produced by the reaction of polyurethanes having urea groups with butane sulphone (lactone of hydroxy sulphonic acid) or succinic anhydride<sup>25,26</sup> (Reaction 5). They can also be produced during polymer synthesis by poly-addition of diisocyanates with diaminosulphonic acids or diaminocarboxylic acids<sup>26-31</sup>.

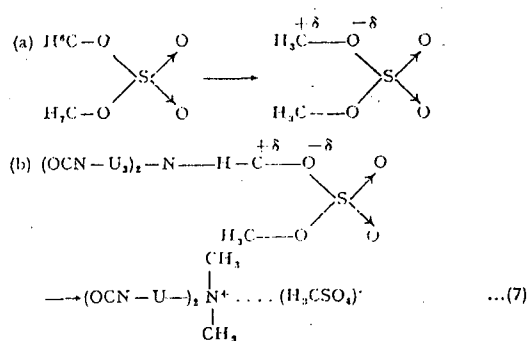


Anionic urethane was also prepared by treating the polymer obtained from alcoholized linseed oil and diisocyanates with maleic anhydride and neutralizing with triethyl amine<sup>32-34</sup>. The coating obtained became dry to touch within 2-5 hr at room temperature in the presence of cobalt naphthanate drier. Similarly, a thermosetting resin can be obtained by reacting NCO-ended prepolymer with trimellitic anhydride, an epoxide and an amine. This is baked at elevated temperature after adding melamine-formaldehyde and water<sup>35,36</sup>.

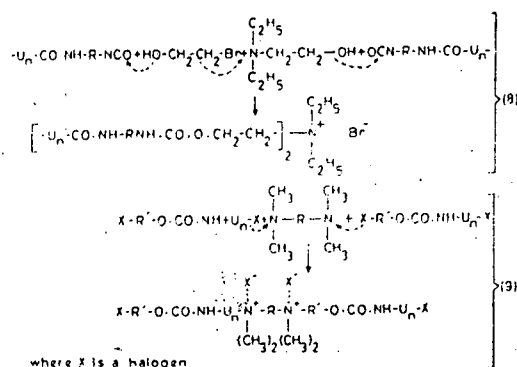
### Cationic Materials

The first water-soluble polyurethanes were cationics. They were made as early as 1942 by Schlack. He reacted 1,6-hexamethylene diisocyanate with N-methyl diethanol amine and got the strongly basic polyurethanes<sup>37</sup> (Reaction 6). They were soluble in dilute formic and acetic acids and/or  $\text{FeCl}_3$  or  $\text{SnCl}_2$  solutions<sup>37-39</sup>. The nitrogen derived from N-methyl-diethanol-amine could be made basic by treatment with dimethyl sulphate or benzyl chloride also (Reaction 7). These polyurethanes were, however, not useful because of their extreme hydrophilicity and low molecular weight.





In the above method, addition of easily quaternizable nitrogen into the polyurethane backbone is the chief step involved<sup>60-62</sup>. For that matter, other quaternizable atoms like phosphorus can and have been tried. Subsequent quaternization of the added nitrogen is the next step in Schalek's method. But polyaddition and quaternization can also be carried out simultaneously. In the reaction of diisocyanates with N-methyl diethanolamine, the envisaged polyaddition-quaternization could be achieved by the use of haloalcohol and a monoalcohol of a tertiary amine in place of the N-methyl diethanolamine<sup>63-69</sup> (Reaction 8). A prominent merit of this method is that it produces polymers of high molecular weight. Yet another way of polyaddition-quaternization has been reported in the reaction of halogen-ended urethane prepolymers with tertiary diamines<sup>70,71</sup> (Reaction 9).



All the cases considered hitherto related only to the elements of the fifth group of the periodic table. By the same criterion, higher group elements may also be used for this purpose. Elements of sixth group, in particular, are worthy of exploitation. Attempts have been made to utilize the base-forming powers of sulphur. Sulphonium ion is formed by ternation in this case<sup>72</sup>. For example, urethane prepolymer obtained from toluene-diisocyanate and polypropyleneglycol ether was chain-extended with thio-diglycol in the presence of dibutyl tin-dilaurate in acetone medium. This was then reacted with dimethyl sulphate in water and the solvent was distilled to obtain a stable latex<sup>73</sup>.

The basic character of all cationic products is usually a function of the basic groups content. Consequently, ionomers possessing a lesser amount of these groups exhibit proportionately reduced solubility. For example, the products—originally obtained by Schlack were soluble in 20% hot acid and on cooling formed a gel. It was noticed that once the content of the basic nitrogen dropped below 1.5%, the polymer no longer dissolved in the hot acid even at higher temperature. However, technically useful ionomers are those in which the basic nitrogen content is just enough to make the polymer insoluble in water and yet soluble in polar solvents containing minor quantities of water. Such systems can be further thinned with water without separation. The organic solvent can be removed later to leave a stable polyurethane latex<sup>74</sup>.

### Properties of Polyurethane Ionomers

The greatest merit of ionomers is that they can be dispersed in water without external assistance. This has several interesting consequences. The absence of emulsifier makes the dispersions less sensitive to mechanical shearing as well as organic solvents, with the result that they can be heated or stirred or even diluted with solvents without causing precipitation. The film-forming properties are also outstanding. Since no problems of compatibility are associated with emulsifiers, the coatings impart high gloss to the substrate. The hardness of the films obtained has been found to be in the range 20-220 sec (the hardness of glass) of pendulum hardness. The films were found to exhibit an extraordinarily high degree of physical crosslinking due to the joint action of electrostatic forces between charged centres and the hydrogen bridges. This physical crosslinking leads to increased water and solvent resistance and higher tensile strength. However, to achieve optimum properties, additional crosslinking is recommended.

Chemical crosslinking can be effected in any one of the following ways. Polyurethane possessing a small quantity of free NCO groups can be crosslinked by reacting with water. While such crosslinks are intra-lattice/particulate in the case of non-ionic lattices (i.e. dispersions containing emulsifiers), in respect of ionomeric dispersions they are both intra- and inter-particulate, predominantly of the latter type. Formaldehyde has been found to be a good crosslinking agent for the ionomers. Crosslinking occurs by the formation of a methylene bridge between urethane groups and is possible both in films and lattices<sup>75,76</sup>. Cationic polyurethanes are crosslinked by means of bifunctional quaternizing<sup>77</sup> agents like 1,4-bis(chloromethyl) benzene and 1,4-dibromobutane. These are first incorporated mono-functionally and crosslinking is effected at a later stage.

Crosslinked ionomers have been found to be highly stable to organic solvents containing water. The polyurethane dispersions are known to form films even in the range of highest surface hardness and in this respect they outdo the hard vinyl dispersions which do not form films. Suitably formulated dispersions after a minimum of drying time are known to exhibit surface hardness in the

range 180-220 sec of pendulum hardness. Despite this higher surface hardness, they exhibit no brittleness, as can be seen from the high abrasion resistance. (They are found to lose only 15-18 mg after 1000 revolutions under 1 kg weight in the Taber abrader.) Their flexibility is also comparable to that of other solvent-based systems, as can be seen from Erichsen cupping values of over 7 mm.

Polyurethane ionomers are characterized by fast drying, permitting recoating of the substrates within a short time. Other advantages include good adhesion to many substrates, such as wood, paper, glass, ceramics, cement, fibreboard, etc., and good resistance to a number of solvents, particularly hydrocarbons. They are also resistant to oils and greases and their water sensitivity has been found to be negligible. While cationic systems were found to be inadequate in respect of light fastness, pigment dispersion and weather resistance, anionic systems derived from aliphatic isocyanates were found to be superior in these respects.

### Conclusion

The increasing awareness about air pollution, fire hazards and discomfort in the use of solvent-based finishes have given impetus to the use of aqueous systems. Although synthesis of polyurethanes directly in aqueous media is not possible, it can be effected by a modified emulsion technique in which one of the reactants is hydrophilic or the reaction is carried out with a urethane prepolymer in the presence of nonionic emulsifiers. But ionomers are more important due to their ability to disperse themselves in the water medium and the high stability of the resulting dispersions against high mechanical shear, heat and ageing. Electrostatic repulsion causing dispersal of the polymeric particles and the non-strippable nature of the incorporation of the groups bearing these charges are responsible for the permanent stability of these ionomeric dispersions. Further, the absence of emulsifiers immediately minimizes the incidence of haze and similarly, gloss, hardness, quick drying, adhesion, solvent resistance, etc. are also more for the ionomeric finishes than for the solvent-based finishes. The infinite scope for variation in the strength, number, kind of charge and compactness of the hydrophilic groups as well as the molecular weight of the polymeric chains and the degree of their crosslinking subsequently have combined to open up a wide range of variations in these properties. High solids content at low viscosity, easy cleaning-up, low cost and other such advantages of aqueous systems—all put together promise continually expanding uses for ionomers.

### Summary

The general methods for the production of non-ionic, anionic and cationic polyurethanes in aqueous medium are reviewed. The properties of the polyurethane ionomers with respect to their dispersibility in water, mechanical shear, heat and ageing are discussed. The scope for introducing variation in the kind of charge and compactness of hydrophilic groups, as well as the molecular weight of the polymeric chains in the ionomers is discussed.

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