CC: G. D. Graves, Wilm. F&F } In
J. B. Bullitt, " " } Turn
D. McBurney, " "
R. E. Thomas, Newburgh
E. A. Rodman, Newburgh
R. B. Davis, Lab.
Russell Morgan, Lab.
P. B. Evans, Lab.
P. Robinson, Lab.
O. H. Bullitt, Exp. Sta., Wilm.
W. D. Lawson, Lab.
H. G. Stauffer, Lab.
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Patent Section, Lab.

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CONFIDENTIAL

Marshall Laboratory
July 15, 1954

MEMORANDUM REPORT NO. M-715

PREPARED BY: H. E. EASTLACK

"ADIPRENE" AS A COATING POLYMER

Introduction:

The writer visited the Jackson Laboratory on July 1 to develop further information on the possibilities of "Adiprene" for coating purposes. Persons interviewed were:

J. W. Libby, Jackson Laboratory
Eric Barthel, " "
J. A. Nelson, " "
E. K. Gladding, " "
J. S. Rugg, Rubber Laboratory

Summary:

From the information obtained, it seems doubtful that it will be possible to prepare coatings from Elastomer N solutions that have all the properties of "Adiprene" rubber stock, unless elaborate precautions are taken to rigidly exclude water, not only from the materials used, but also during the curing operation. Nevertheless, films cured in contact with atmospheric moisture may still be sufficiently tough and abrasion resistant to be of interest for coatings.

A more likely approach to coatings that can be applied by practical means appears to lie in the use of the "prepolymer", or a recently developed latex. Tough, abrasion resistant films can be prepared by rather simple techniques from the prepolymer. Such films cure by reaction with water in a humid atmosphere, or they can be cured by passing through a diamine bath. The latex deposits a film which is similar chemically to uncured Elastomer N, but higher in molecular weight. Tough, rubbery films are obtained without curing, or they may be cured by passing through a TDI bath.

Action:

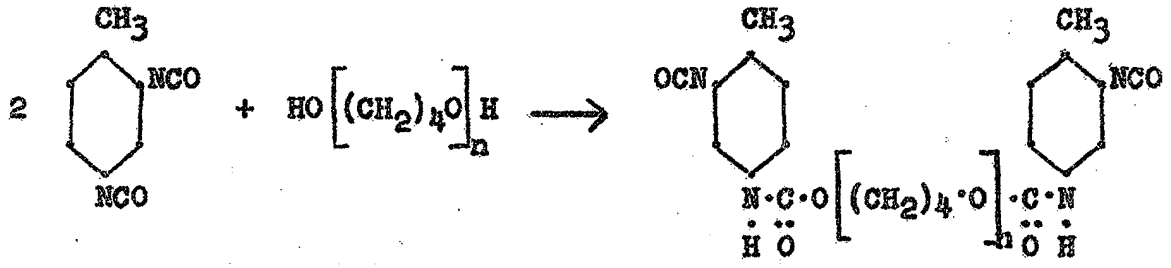
1. H. G. Stauffer and the writer will undertake to characterize films from solutions of Elastomer N, the prepolymer, and the latex.

2. Newburgh's attention is called to the possibility of using the prepolymer or the latex for fabric or webb coating.

Discussion:

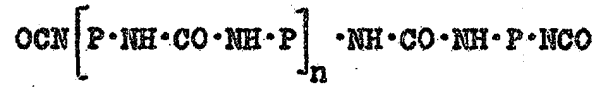
Chemistry of "Adiprene" (Confidential):

The first step in producing Elastomer N ("Adiprene" Rubber Stock) is to prepare a "prepolymer" by reacting toluene diisocyanate (TDI) with a polytetramethylene glycol having a molecular weight of about 3000:



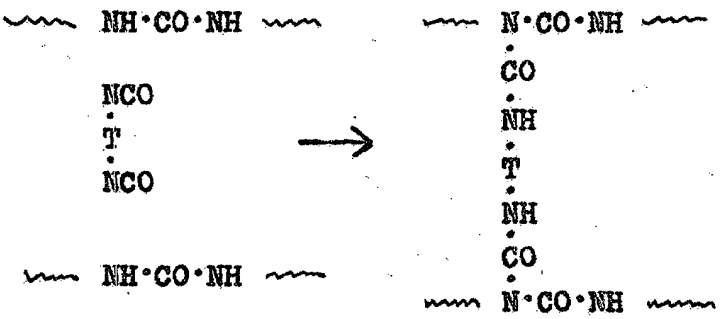
Prepolymer (TGT)

The prepolymer (OCN-P-NCO) is then reacted with water to extend the chain length and to produce an unstablized polymer:

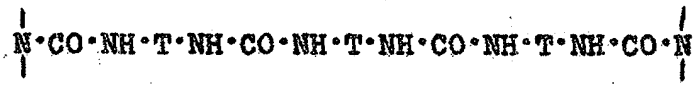


This is stabilized by terminating the chain with piperidine to produce Elastomer N (mol. wt. 30,000). Elastomer N, contains 1% of phenyl β naphylamine ("Neozone" D) as an anti-oxidant. Other elastomers can be prepared by using different polymeric glycols, and by extending the prepolymer chain length with diamines. However, Elastomer N (water extended) appears to be the one on which Orchem is concentrating most of their effort.

Curing of Elastomer N with TDI takes place by reaction of the -NCO groups with the $-NH_2$ groups. Under anhydrous conditions the reaction may be represented as fololws:



In the presence of water, some of the TDI reacts with itself to produce longer crosslinking chains, e.g.,



The polymeric structure obtained in the presence of water is therefore different from that obtained under anhydrous conditions.

Preparation of Films from Elastomer N Solutions:

Elastomer N picks up 1-2% of water under normal storage conditions and should therefore be dried before use, by milling for 10-20 minutes on a 2-roller mill.

The disappointing results of Marshall Laboratory work with films sprayed from solutions of Elastomer N in dimethyl formamide (DMF), may have been due to (1) the fact that the Elastomer was not dried, (2) the effect of atmospheric moisture, (3) the DMF was not redistilled to remove traces of amines, and (4) DMF reacts with TDI.

Tetrahydrofuran (THF) is a better solvent for Elastomer N than DMF, particularly when mixed with either chloroform or dichloroethylene. The THF should be absolutely dry, free from peroxides, and the stabilizing agent present in the material as supplied by Elchem must be removed.

TDI-urea (OCN·T·NH·CO·NH·T·NCO) is a better curing agent than TDI, producing tougher films, but is insoluble in THF. It was suggested that we try both TDI (in solution) and TDI-urea (in suspension), using 4 and 8 parts per 100 parts of Elastomer N.

Knife coating was suggested in preference to brushing or spraying to minimize contact with atmospheric moisture. Flash drying should also be carried out under conditions involving minimum exposure to moisture.

Curing for 15, 30, and 60 minutes at 130°C. and 5-15 minutes at 110°C. was suggested (shorter curing time results in a higher modulus). Films should be aged 1-2 weeks at >50% R.H. before testing, to allow for "after curing". Note: TDI is very toxic (maximum safe concentration: 0.1 p.p.m.). Hence it should be handled with extreme care, and curing ovens should be vented to the outside.

Reinforcing agents may yield tougher, more abrasion resistant films. HAF carbon black, and Cab-O-Sil (SiO_2) are best. From 15 to 30 parts per 100 parts of Elastomer N were suggested. The Elastomer should first be warmed up on a rubber mill before adding the extender. The stock is removed from the mill at intervals, allowed to cool and the operation repeated until a cut surface is glossy.

The Tabor abrasion test does not measure resistance to abrasion as related to tire wear. All Jackson Laboratory tests for this service are made by road-testing tires.

Use of "Prepolymer" as a Film Former:

The prepolymer, as described above, reacts rapidly with water and must therefore be kept absolutely dry until used. Jackson Laboratory will supply samples blanketed with dry nitrogen in sealed bottles. Once opened the entire sample should be used immediately or discarded.

The prepolymer (TGT) is a liquid having about the consistency of honey. It contains some free TDI. Films can be made by knife casting without dilution. It is readily miscible with THF, or with a 50/50 mixture of toluene and either MEK or MIBK. From 10-20 parts of solvent should be sufficient to reduce TGT to brushing consistency; 20-30 parts, to spraying consistency. The latter two methods of application will, of course, involve more contact with atmospheric moisture before the film is laid down, than knife coating.

Films of TGT cure in 1-4 days at 50% R.H. and 80°F., but at least 7 days should be allowed before testing the film. Such films are comparable with nylon in the Tabor abrasion test. TGT films can also be cured by contact with diamines, e.g., m-phenylene diamine.

"Adiprene" Latex:

A latex has been prepared by dispersing the prepolymer in water. Reaction of the water with the terminal - NCO groups extends the chain to form a polymer similar chemically to uncured Elastomer N, but higher in molecular weight. When this polymer is separated from the latex by filtration, washed to remove water soluble dispersing agents, and dried at room or slightly elevated temperatures, a tough rubbery film is obtained. It can be cured, if desired, by dipping in a solution of TDI.

It should be possible to prepare films from this latex by casting on glass, or spreading on fabric or other substrates. A sample is being obtained for evaluation along this line. The film forming properties of this latex are said to be much better than those of the amine-extended latex of which we previously had a sample.

H. E. EASTLACK

HEE:AUB
7-14-54

P.S.

The following two reports have been received and turned over to the Marshall Laboratory Library:

Haskell Laboratory: "Report on the Toxicity of Toluene - 2,4-Diisocyanate (TDI)",

Rubber Laboratory: "A Procedure for Determining the Concentration of TDI and TDI-Urea in Air".