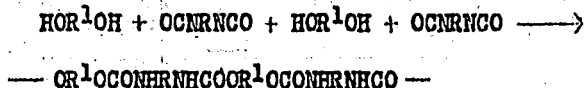


Frankfort - September 24, 1941

### FOLYURETHANES

A polymerization reaction which combines the possibilities and advantages of condensation polymerization with those of polymerization by addition and which, therefore, makes it possible to obtain by pure addition reactions predetermined final products from any bi- and polyfunctional low-molecular compounds or preliminary condensates and polymerizates has been found in the polyurethane polymerization or "diisocyanate process". This reaction was found in 1937 and has been further developed since that time.

Wurtz had found, in 1848, that  $C_2H_5NCO$  adds easily to  $C_2H_5OH$  and thereby gives  $C_2H_5NHCOOC_2H_5$ ; reaction with  $RR_1NH$  yields  $C_2H_5NHCONRR_1$ . The same reaction, as is well known, takes place with phenylisocyanate. In order to adapt this reaction which proceeds quantitatively and exothermically to the purposes of the chemistry of plastics it was necessary to prepare diisocyanates and to add these on to glycols, diamines, polyhydroxy or polyamino compounds. As can be seen from the simplest reaction of this kind, the reaction of diisocyanate with glycol, this reaction can be considered as largely analogous to the pure polymerization reaction.



A considerable difference, as compared to the known polymerization processes consists in the fact that the molecular bonds are not exclusively those of carbon atoms but also those between oxygen, carbon and nitrogen, and considering the enormous number of only the polyhydroxy compounds, it can be easily seen how generally applicable this reaction is. Neither with the known condensation nor the known polymerization processes can such a breadth of application be covered.

After the work of Carothers on super-polyamides had become known, the I. G. found it necessary to prepare similar or, if possible, better compounds which were independent from the Du Pont patents.

The addition of diisocyanate to diamines and glycols has, consequently, been intensively investigated in order to prepare high-molecular linear polyureas and polyurethanes. It was found that when long chain aliphatic diamines and aliphatic diisocyanates are used, only high-melting and highly hydrophilic polymers result which cannot be used in the fusion-spinning process and, therefore, are of no practical importance for the industry of synthetic fibers. However, a basic polyurea prepared in this way is being used commercially as animalizing material for rayon made by the copperammonium salt process.

On the other hand, the linear polyurethanes were found to be a synthetic material of many uses with properties which partly surpassed those of the super-polyamides. Of the great number of linear polyurethanes prepared, a few should be mentioned. From a technical standpoint, one of the most easily obtained compounds of this kind is the polyurethane from 1,6-Hexanediisocyanate and 1,4-butylene glycol:



This material was found suitable for the manufacture of silk, plastics and, especially, bristles. It is prepared commercially by the addition of 1 mol. of the purest 1,6-hexamethylenediisocyanate to 1 mol. of 1,4-butyleneglycol in monochlorobenzene solution. The reaction is strongly exothermic (374 B. t. u. per pound of polyurethane). After a reaction time of about 1 hour the polyurethane separates in the form of a fine, sandy powder in practically quantitative yield. Depending on the reaction temperature and the residence time in the solution which can be controlled by the addition of dichlorobenzene, or by breaking the chain with monofunctional compounds, it is possible to synthesize polyurethanes of varying degrees of polymerization.

The properties and characteristics of a polyurethane of this type which is marketed as "Igamid U" for plastics and as "Perlon U" for silk and bristles are given in the following tabulation.

Physical Properties of Igamides

	<u>Igamid U</u>	<u>Igamid A</u>	<u>Igamid B</u>
Sp. Gravity $\frac{20^{\circ}\text{C.}}{4^{\circ}\text{C.}}$	1.21	1.14	1.15
Melting Point, approx.	183°C.	255°C.	210°C.

Injection molded material

Brinell hardness at 60°C. (kg/cm <sup>2</sup> )	750	1000	600
Band-drop test (cm.kg/cm <sup>2</sup> )	about 100	over 100	--

Pressed material

a) unoriented plates

Rupture strength (kg/cm <sup>2</sup> )	620	No	380
Resistance to cold	+8°C.	pressed	+13°C.

b) oriented plates

Rupture strength (kg/cm <sup>2</sup> )	lengthwise	1874	can	1050
	sidewise	1100		860
Rupture elongation (%)	lengthwise	60	be	70
	sidewise	81	made	73
Resistance to cold		-30°C.		-30°C.

Because of its preparation (polymerisation in solution and precipitation after reaching a definite degree of polymerization) "Igamid U" is more uniform as a polymer than the super-polyamide obtained by condensation (Nylon). This is shown, e. g., by the close proximity of the softening and the melting point.

From all the commercially important spinnable and linear super-polymers, "Perlon U" has the lowest melting point, approximately the same as acetate rayon, which is important for a number of textile uses.

The strength of the artificial silk and bristles made from the polyurethanes is practically identical to that of the super-polyamides. In the laboratory, maximum strength values up to 7.5 grams per den. were found for "Perlon U" as compared to natural silk with 3.5 grams per den. It is possible, therefore, to obtain threads which exceed the strength of the best natural silk by about 100%.

Especially characteristic for "Igamid U" and all other polyurethanes is their low water absorption. By increasing number of  $\text{CH}_2$  groups in the polyurethane chain, the water absorption is still further decreased but, at the same time, strength and melting point decrease since the molecules become more and more paraffin-like. With regard to electrical properties and resistance to weather, the polyurethanes surpass the polyamides. Furthermore, they have an increased resistance to acids.

These special properties in conjunction with the other good properties of the super-polyamides make "Igamid U" valuable as thermoplastic. The materials prepared by injection molding are resistant to water and moisture of the air and remain constant in their dimensions. All these properties are valuable for the manufacture of filter cloth resistant to boiling water and acids, acid- and gas-resistant suits, belts, ropes, cable insulation, et cetera. In the textile field the low-water absorption of the polyurethanes is of advantage in the manufacture of hosiery but is a disadvantage for underwear.

"Perlon U" is a valuable material for the manufacture of bristles and artificial horsehair because of its hardness, its elasticity which is similar to metal strings, and its resistance towards atmospheric moisture up to about  $176^\circ\text{F}$ . "Perlon U" is distinguished from the super-polyamides by its behavior towards dyes. Since it does not contain any basic groups, it cannot be dyed with acidic dyes but only with dyes for acetate rayon or suspension dyes. Also, because of the lack of basic groups, "Igamid U" is considerably less susceptible to the oxygen of the atmosphere when molten as compared to the super polyamides and brown discoloration of the material on melting, molding and spinning does not take place even when air is not completely excluded.

Besides "Igamid U" and "Perlon U", the following types will become commercially important:

The polyurethanes prepared from 1,4-butanediisocyanate and 1,4-butylene-glycol. It has practically the same properties as "Igamid U" but melts about  $24^\circ\text{F}$ . higher (melting point  $194^\circ\text{C}$ .,  $(381^\circ\text{F})$ ). It will probably be cheaper than "Igamid U" and is prepared from acetylene and HCN with 1,4-diaminobutane as intermediate. In this way it is possible to eliminate phenol or benzol as raw material bases.

Different from these uniform polyurethanes whose lower molecular weight members are completely insoluble in all solvents in the cold and which are only soluble in a phenol-water mixture (80 : 10) are the compounds prepared from a mixture of glycols or diisocyanates; these compounds are easily soluble in chlorinated hydrocarbons even in the cold, have a lower melting point, a greater thermoplastic region, greater softness and better compatibility with plasticisers.

They are, therefore, suitable raw materials for the manufacture of film, foils and leather substitutes.

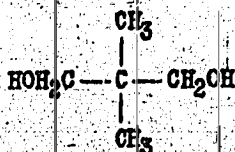
"Igamid U" in which only 10 mol-percent of butyleneglycol is replaced by methyl-1,6-hexanediol is considerably more thermoplastic and thereby easier to mold than the uniform material. It is, furthermore, important that it can be prepared without solvents, simply by fusion of the components.

For practical purposes it was found unimportant which of the glycols are polymerized in mixture with the inexpensive 1,4-butyleneglycol. As a leather substitute, "Igamid UL" has been considered for manufacture which is a mixed polyurethane which has been made by fusion of 1 mol. of 1,6-hexanediisocyanate and 0.5 mols. of 1,4-butyleneglycol + 0.5 mols. of methylhexanediol. A mixed polymerizate with quite similar properties can be, e. g., made from 0.5 mols. of 1,4- + 0.5 mols. of 1,6-diisocyanate and 0.8 mols. of 1,4-butyleneglycol + 0.2 mols. of methylhexanediol. "Igamid UL" is a very soft material which is easily soluble in mixtures of chloroform and alcohol. In many of its properties it is considerably superior to leather. It is especially suitable as a leather substitute because it is practically without sensitivity to water and, consequently, does not break at extreme dryness or on heating in water.

#### Physical Properties of Igamides for Leather Substitutes

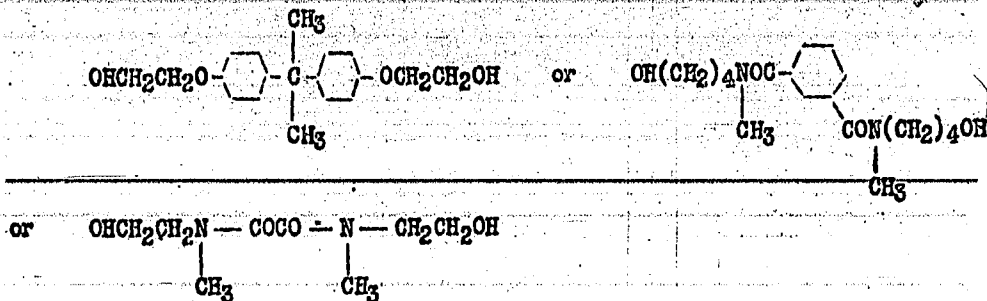
	<u>Igamid UL</u> <u>40% plasticizer</u>	<u>Igamid 6A</u> <u>20% plasticizer</u>	<u>Leather</u>
Rupture strength (kg/cm <sup>2</sup> )	lengthwise 470 sidewise 360	338 186	250
Percent elongation on rupture	lengthwise 243 sidewise 318	191 340	-
Hardness (ball pressure, 60°C., kg/cm <sup>2</sup> )	280	240	-
Resistance to Flexing (no. of flexions)	326000	120000	specified; more than 20000
Loss by abrasion	0.28	0.7	1
Resistance to breaking of stitched material (kg/mm <sup>2</sup> )	lengthwise 11.0 sidewise 13.6	8.1 13.4	10
Behavior towards boiling water	resistant	not resistant	-
Behavior towards dry atmosphere	resistant	breaks easily	-

Because of its elastic properties the polyurethane made from 1 mol. of 1,6-diisocyanate + 0.5 mols. of 1,4-butyleneglycol + 0.5 mol. of



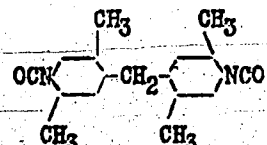
is especially well suited for the impregnation of fabrics. Other interesting types of polyurethanes which are still in the development stage are partly made from the

cheaper aromatic diisocyanates and aliphatic glycols or from aromatic glycols with heteroatoms, e. g.,

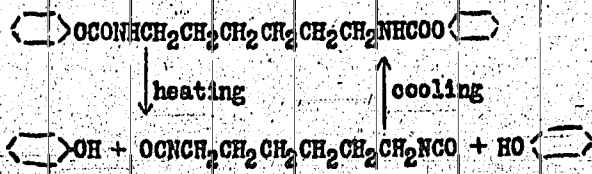


or from aliphatic linear polyesters with three hydroxy groups. These materials can be used as foils for electrical insulating purposes, sausage casings resistant to boiling, carrier materials for photographic film and similar purposes. (Several pages of the report are missing in the microfilm. The missing section deals with the use of diisocyanates in lacquers.)

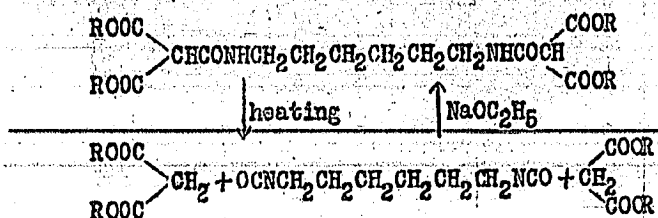
For the use in lacquers the following commercially available diisocyanates should be considered which in the following table are arranged according to their reactivities:

- decreasing reactivity ↓
- 1.) 1-chlorophenylene-2,4-diisocyanate
  - 2.) m-tolylenediisocyanate
  - 3.) 1,6-hexanediisocyanate
  - 4.) diisocyanate from dianisidine, m.p. 126°C. (0.5 mol. cryst.  $\text{C}_6\text{H}_5\text{Cl}$ )
  - 5.)  m.p. 129°C.

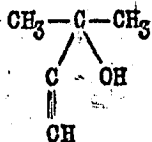
The question of stability of lacquers formulated according to the new process can also be considered from another point of view. It is possible to use, instead of the diisocyanates, compounds which react in the heat like diisocyanates, i. e., they are decomposed under formation of diisocyanates. Compounds in this class are, e. g., the diphenylurethanes which can be prepared either from diisocyanate and phenol or from the phenylester of chloroformic acid and a diamine.



Another group of compounds is also suitable for the same purpose. This group consists of the addition compounds of diisocyanates and malonic esters or acetoacetic ester



which also are decomposed on heating. Other suitable, easily decomposed compounds can be made from the diisocyanates and phenylmethylpyrazolon, diphenylamine or



Another compound can be made from hexane-1,6,-diisocyanate + 1 mol. of ammonia.

These "camouflaged" diisocyanates have the great advantage that lacquer formulations in which they are present can be stored for unlimited periods of time. Solvents containing hydroxy groups can be used with them since these solvents usually evaporate before decomposition to the diisocyanate takes place. The disadvantages of this type of formulation are the necessity to operate at higher temperatures and the fact that undesirable decomposition products are formed. It was found, however, in larger-scale experiments that e. g., the phenol formed or malonic ester formed, as well as their decomposition products, evaporate when the lacquer is burned in.

The following compounds have been found to be useful because they can be manufactured cheaply:

1. A hydrolyzed, mixed polymerizate of 80% vinylchloride and 20% vinylacetate;
2. A polyester containing hydroxy groups obtained by esterification in vacuum of about 3 mols. of adipic acid or thiodipropionic acid, phtalic acid, etc. and 4 mols. of trimethylolpropane, 1,2,4-trihydroxybutane, etc. By blending the acid components it is possible to vary the elasticity within wide limits.
3. The "Luphenes";
4. Benzylcellulose;
5. Condensation products of the esterglycols, according to paragraph 2, + oxygen containing xylolformaldehyde resins.

These new-type lacquers have properties which can be summarized as follows:

1. As compared to the alkyd lacquers, they can be burned in at considerably lower temperatures, partly already at room temperature and are, therefore, suitable for lacquering of paper, textiles, leather, wood, rubber goods, plastics, et cetera, for which a suitable material was not available up to now.
2. Their properties can be varied in a way which was not obtainable with other lacquer materials.
3. They show unusual adhesion to the surface and, consequently, very high gloss and, in most cases, are resistant to low temperatures. They are water resistant and are able to bind pigments; their resistance to weather and solvents is excellent.
4. They have high electric resistance (specific resistance -  $10^{15}$ - $10^{16}$  Ohm per centimeter) because the diisocyanate groups react with all reactive hydrogen atoms which cause electric conductivity. They are also remarkably resistant to creep currents which is of special importance in the manufacture of cable lacquers.

The new lacquers have the following disadvantages:

1. Low stability of the finished lacquer solutions. They must be used up in one day.
2. The necessity of using solvents without hydroxy groups and the requirement of the complete absence of water.
3. The sometimes sharp odor of the low molecular weight diisocyanates.

The good adhesion, the high elasticity and the resistance to boiling water of some of the isocyanate lacquers appear to make them especially suitable for the coating of tin cans. Since resinification takes place without the liberation of reaction products, the coatings have high impermeability to gas. The resistance to mustard gas of diisocyanate lacquers exceeds that of Oppanol.

The fact that the introduction of urethane groups imparts high water resistance to materials and also that the linkage of the molecules by means of diisocyanates represents a very mild building principle led to experiments to improve linseed oil by this new method.

Linseed oil was esterified with the calculated amount of glycerine or trimethylolethane to form the diglyceride and to the latter was then added 0.5 mols. of chlorophenylenediisocyanate which resulted in the formation of a molecule containing 4 drying fatty acid radicals.

These diisocyanate-linseed oils have a number of interesting applications in the field of rust protection, the manufacture of oiled silk, lacquers for electrical insulating purposes, airplane lacquers, and it is even possible by this method to obtain rapidly and completely drying oils from oils with poor drying properties like train or sardine oils.

In this way oils of any desired viscosity can be prepared depending on the degree of esterification without having to expose the oils to drastic thermal treatment like boiling at a temperature of 536°F. as practiced in the case of boiled linseed oil or certain alkydals.

A modified linseed oil prepared in this way considerably surpasses the properties of oxidized linseed oil, dries fast and completely, gives films of higher elasticity, reaches water resistance quickly and is very compatible with basic pigments with which it does not thicken.

Its resistance to light is somewhat less than that of oxidized linseed oil.

For the manufacture of thermosetting plastics, the diisocyanate is mixed with the polyhydroxy compound in approximately molar ratio of the reactive groups, larger amounts of fillers, e.g., wood dust, are added and the mixture of the two components is reacted under heat and pressure similar to the manufacture of pressed materials from bakelite or urea resins. The limited stability of the diisocyanate-polyalcohol mixtures is a disadvantage. If insufficient care is taken the two components react already on the rolls of the mill during mixing. The raw materials for these purposes are, therefore, limited to the slowly reacting and high melting diisocyanates from dianisidine and di-p-xylylidinemethane with which quite good results have been obtained when they were used with, e.g., a polyester from adipic acid and trimethylolethane similar to the ester used in lacquer formulas. At temperatures of 284 - 520°F. and a press time of 5-10 minutes, materials are obtained which have the following advantages:

1. High resistance to alkalis;
2. High electric resistance (3 - 5,000,000 megohms as compared to 20,000 megohms for bakelite);
3. High resistance to creep currents even when moist;
4. Much easier flow than bakelite masses which permits the manufacture of pressed articles of 3 times the weight of those made at present from phenolformaldehyde resins;
5. The most important property of the new materials is their high elasticity as indicated by increased drop-flexibility. This appears to be the solution of the problem of an "elastic bakelite". Similar as in the lacquer field, here, also, the possibility is given to obtain materials with higher surface hardness by the use of predominantly aromatic components, whereas softer and highly elastic materials are obtained when predominantly aliphatic components are used. A simplification of the manufacturing process seems to be possible since the plastic powder can be shaped cold and subsequently be baked in a furnace without the use of pressure. Resinification takes place so rapidly that no deformation and change in dimensions occurs.

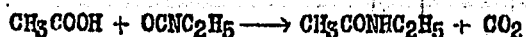
Materials of this sort will be useful in the manufacture of load-carrying construction parts for airplanes and for large structures for which metal cannot be used and for which bakelite is unsuitable because of its lower strength. The new preparations might also be used to replace the formaldehyde plastics made with the addition of furfural derivatives which are used for the manufacture of grinding wheels.



The use of "Cellit" as a polyhydroxy compound has been investigated thoroughly and it was found that infusible pressed products which can be removed hot from the mold are obtained by reaction with diisocyanates.

By means of diisocyanates it is also possible to manufacture insoluble and infusible acetate rayon. Since "Cellit" is spun from an alcohol-acetone solution, it is advantageous to use compounds which on heating to about 266°F. split off diisocyanates which subsequently react completely with the long cellulose chains.

The isocyanate group does not only react with hydroxy and amino groups but also with carboxylic groups according to the following equation:



This reaction can be used for the manufacture of novel and very strong foam-type materials. If, e.g., a polyester made from a dicarboxylic acid and a 3-valent alcohol and which still contains both free hydroxy groups and free carboxylic groups is brought together with a diisocyanate, the honeylike mass begins to react at about 50°C. (122°F.), forming urethane and carboxamide bridges under simultaneous elimination of CO<sub>2</sub>. The whole mass rises like dough and solidifies with increasing resinification. In this way it is possible to manufacture foam-type materials of very high strength and any desired degree of elasticity. A material which, e.g., has a pressure resistance of about 10 kilograms per cubic centimeter and also satisfactory heat resistance up to 100°C. (212°F.) is made from tolylenediisocyanate and a polyester from oxalic acid, adipic acid and trimethylolethane; it has a specific gravity below 0.1.

At present the German Air Force is extremely interested in this material for the manufacture of unsinkable airplane parts. Because of its great strength the foam material can be used simultaneously for load-carrying construction parts. It is superior to balsa wood used by the Americans. The new material is also well suited for insulation for low temperatures.

When it was attempted to replace vulcanization of the Buna type of synthetic rubber by the addition of diisocyanates to mixed Buna polymerizates containing hydroxy groups or to polyisobutylenes containing hydroxy groups, it was found that Buna-S already shows a definite vulcanization effect after treatment with diisocyanates. Whether the slight oxygen content of Buna or the reactive double bonds or CH<sub>2</sub> groups are responsible for this phenomenon has not yet been cleared up. It was found that these vulcanizates adhere extremely strongly to the metal parts of the vulcanizing press. The practical utilization of this phenomenon gave the long-sought adhesive for Buna. By means of diisocyanates it was possible to obtain temperature-resistant laminates of Buna-sulphur mixtures on iron, light metals, porcelain, et cetera, which showed a strength up to 80 kg/cm<sup>2</sup>. The diisocyanates of m-tolylenediamine and hexamethylenediamine were found especially suitable; these materials are commercially available as "Vulkollan-T" and "H". Only by means of these materials is it today possible to manufacture tank tread supports and satisfactory laminates of rubberized materials without the use of natural rubber.

In Leverkusen an investigation is under way to build tires by means of these "Vulkollans" using metal cord and rubber; up to now, this had not been possible mainly because of the low adhesion of rubber to metal. If the solution of this important problem is successful, the highly heat-resistant and continuously retreadable tire for the cheap automobile has been found.

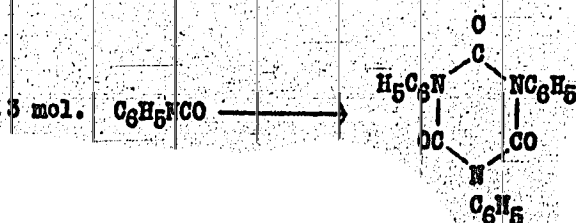
The good adhesion of the Buna diisocyanate mixtures makes possible the manufacture of a new construction material for airplanes which has been proposed by the Gotha Waggonfabrik; this material consists of a thin laminate of Vulcanized fiber and a light metal sheet. It was found that the Vulcan fiber or the metal broke before the lamination could be ruptured. This material which consists on the outside of light metal and on the inside of cellulose makes it possible to build a metal airplane by wood construction methods. This would mean that the construction time for a heavy bomber could be out to about 1/3. At the same time the new material would have a higher resistance to enemy bullets than the light metal sheets without support. After the war this construction material should be found useful for automobile bodies. Vulcan fiber with a coating of synthetic rubber would be an interesting material for the manufacture of suitcases for the tropics. The Buna isocyanate laminate can also be used in the field of synthetic rubber springs.

The diisocyanates were generally tested for their suitability as adhesives. It was found that by means of these compounds it was possible to solve adhesive problems which up to now could not be solved successfully. It was possible, even in the cold, to cement Oppanol sheets to iron or wood using a polyester as adhesive. The laminating of thin sheets of vulcan fiber to give thick plates was also possible and these plates were equivalent to the thick vulcan fiber plates which required manufacturing processes extending over several years.

Laminating of sheets of paper by means of diisocyanates alone or together with a polyalcohol gives a material which, in all its properties, is equal to vulcan fiber. It was even possible to cement metal to metal by means of these compounds which, again, is important for the mass production of airplanes.

The chemistry of the interesting cementing effect can be explained as follows:

1. The diisocyanates react with the oxide hydrate layers on the metal surface, thereby creating bright surfaces; the residual valences of the metal lattice and the urea groups form a bond which possibly corresponds to a chemical bond but can be at least considered as a secondary valence bond.
2. The diisocyanates are soluble in most organic materials.
3. The diisocyanates easily polymerize in the presence of metals, especially iron compounds or basic materials like phenolates and pyridine, to give high-molecular materials and so form many connective tridimensional triazine rings. Even the monofunctional phenylisocyanate is easily converted into the corresponding trimeric compound:



By means of the diisocyanates it was possible to satisfactorily solve the problem of manufacturing an animalization agent for copper rayon. It was found that an animalization agent which permits to dye cellulose threads with acidic dyes must have the following properties:

1. Extremely large molecules with definite absorption properties.
2. The basic nitrogen, which is responsible for the binding of acids, must not represent more than 3% of the molecule.
3. Complete insolubility of all salts even in boiling water.
4. Complete absence of color, no brown discoloration on exposure to light; the resistance to light of acidic dyes must not be affected.
5. The animalization agent must be present in the smallest possible dispersion.

Subsequently, a pigment was developed which consisted of a basic polyurea made by the mixed addition of chlorophenylenediisocyanate + 8, 8<sup>1</sup> - di(amidopropyl) - methylamine to any diamine desired.

The diisocyanates made it possible to prepare waxes which are hydrophobic and at the same time insoluble in gasoline. A water-repellant impregnant which is under development consists of a wax which has been made from 1 mole of 1,6-hexanediisocyanate + 2 moles of a mixture of higher fat alcohols (C<sub>12</sub>-C<sub>18</sub>); this material is used together with zirconium oxychloride and some Kaurit.

The raw materials necessary for the manufacture of the polyurethanes are diamines, phosgene, glycols and polyhydroxy compounds.

For the manufacture of linear polyurethanes, mainly 1,4-butyleneglycol and methyl-1,6-hexanediol are used. 1,4-butanediol is now very cheaply available commercially by the Reppe synthesis from formaldehyde and acetylene. The methylhexanediol is prepared by hydrogenation of a mixture of the esters of crude methyladipic acid which is obtained in Leuna by oxidation of a mixture of cyclohexanol and methylcyclohexanol. The dimethyl-1,3-propanediol can be obtained from isobutyraldehyde and formaldehyde with subsequent hydrogenation. The introduction of other methyl groups or longer side chains gives linear polymers whose strength and melting points are already considerably lower.

The raw materials for the diisocyanates are the corresponding aliphatic and aromatic diamines which are converted into diisocyanates by means of phosgene:



Of the straight-chain diamines, the 1,6-hexamethylenediamine is easily available by the well-known process in which adipic acid dinitrile is hydrogenated. However, attempts are being made to start with 1,4-diaminobutane since this can be made cheaper from acetylene and HCN which would mean independence from phenol and benzol. This is based on the fact that it has been found that acrylonitrile can be made directly from acetylene and HCN by means of copper chloride catalysts and that the nitrile adds another mole of HCN in the presence of alkaline catalysts.

The succinic dinitrile obtained can be hydrogenated under very mild conditions to 1,4-diaminobutane. The aromatic diamines are dyestuff intermediates which have been known for a long time.

The conversion of the aliphatic diamines into the diisocyanates can be carried out by means of phosgene in various ways. The chlorhydrate of the bases suspended in dichlorobenzene can be treated with phosgene continuously or discontinuously and gives a yield of over 80% of the theory of purest diisocyanate. For the commercial process, however, it is intended to pass the free base into a mixture of dichlorobenzene and phosgene whereby, probably, first the hydrochloric acid salt of the aminocarbamic acid chloride is formed,  $\text{HClNH}_2(\text{CH}_2)_6\text{NHCOC}_2\text{H}_5$ , which can be further reacted with phosgene without difficulty. The preparation of pure diisocyanates has, at first, been very difficult since these compounds are very sensitive and polymerize easily. The conversion of the aromatic diamines into the diisocyanates is very easy. The low-molecular weight compounds can be distilled, whereas the diisocyanates with 2 benzene nuclei cannot be distilled on a large scale but in some cases they separate practically quantitatively from the chlorobenzene subsequent to the treatment with phosgene.

It is assumed that the linear polyurethanes will be produced at the same price as the polyamides; the polyurethane leather which is made in the molten state can be produced cheaper than the competitive polyamide material.