

TRANSLATION
OF
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Reel-18
Dr. R. Rosen
Std. Oil Dev. Co.

B/M

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Polyurethane
by: O. Bayer

SUMMARY (INDEX).

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6. Pressed masses.
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10. Diisocyanates as adhesives.
11. Animalizing agents.
12. Gasoline-proof and laundry-proof hydrophobing.
13. Production of the starting materials.

*Leverkuser I. G. Werke Vertrag: gehalten
auf der T. A. Sitzung zu Frankfurt a. M.
9/24/41.*

9 66.67 - 30.7

TRANSLATION

from:

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POLYURETHANES.

High molecular compounds are, as is well known, produced, in accordance with two basic processes, either by condensation or by polymerization.

The characteristic features of the condensation process are:

1) A large number of small molecules with at least two functional groups each, react together with the release of a low molecular "reaction partner" as for instance water, hydrochloric acid, NaCl, alcohol and the like.

2) For the obtaining of the macromolecular condition, frequently very robust ^{conditions} conditions are applied, as for instance high temperatures, condensation agents, etc. On account of this the plastics obtained are in most cases mixtures of the most varied condensation stages.

3) Valuable and remarkable for the condensation reaction is the possibility of being able to obtain separately any desired intermediate condensation stages and let them possibly come to a final reaction with permanent forming (molding) up to the final stage either as a pressing product, molding resin, or unmeltable varnish coating or finish.

Also mixed condensates can be produced from the most varied preliminary condensation products.

Typical condensation products from the series of the 2-dimensional linear high polymers are, for instance, the 2

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Thiocols from $\text{ClCH}_2\text{CH}_2\text{Cl} + \text{Na}_2\text{S}_4$, the superpolyarides which are produced by condensation from adipic acid and hexamethylenediamine with a molecular weight of 10-20,000; furthermore, in order to mention a few examples from the Group of the most important 3-dimensional, i.e. completely ~~reticulated~~ ^{reticulated} plastics: the hardened bakelite resins, the urea formaldehyde resins, the glyptals and others.

Differing from the condensation process the essential characteristic of the polymerization reaction is the following:

1) The apparently smooth adding-on (bonding) of many molecules (up to about 5000 in linear structure) of monomer compounds to the high molecular polymerisate. This has the same percentage composition as the monomer. The polymerization is an extremely sensitive reaction which, in all probability, is brought about by a shifting of an activated hydrocarbon atom from molecule to molecule of the monomer. It takes place in contrast to condensation in an extremely mild manner. From a kinetic point of view it is a pure chain reaction.

2) Typical for the polymerization reaction is furthermore the fact that one can always only get hold of the final product of a polymerisation and that it is not possible as in the case of the condensation reaction, to obtain separately still reactive intermediate stages or to start from di-, tri- or tetramers and to polymerize same furthermore with each 3

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from:

other or with the monomers into high polymer compounds. In contrast to this such intermediate stages in isolated form frequently even prove to be "polymerization poisons" as is, for instance, the case in connection with the polymerization of isobutylene to copanol.

3) A further essential characteristic feature of the polymerization is that one can start for all practical purposes only with reactive vinyl compounds or dienes and obtain from same either straight line or reticulated polymers which are all produced by direct carbon - carbon linkage. The mixed polymerization of two or three different compounds capable of polymerization it is true, makes possible far-reaching variation possibilities (Igolite, Buna, etc.) but excludes for all practical purposes the high molecular structure via hetero-atoms. In very few exceptional cases it is true, pure polymerization reactions via hetero-atoms have become known. We may mention here the polymerization of strongly tensioned ring systems, for instance ethylene oxide, ethylenimine and caprolactam, and also call attention to the vulcanization of rubber which, as a matter of fact, one must also explain by a further polymerization with reticulation between the linear rubber molecule and the sulfur molecule.

Although in accordance with these two basic reactions an amazing multitude of our plastics are produced, there is

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strong generations of heat for the chemistry of plastic products, it became necessary to ^{use} diisocyanates and to add some to glycols, diamines, polyoxy- or polyamine compounds. You will note already from the simple reaction diagram of a diisocyanate with a glycol that we are confronted here with a reaction which can be compared to a far-reaching extent with the pure polymerization reaction.

Mechanism of the polyurethane formation



An essential difference as compared with the customary polymerization processes consists, however, therein that the molecular linkages are not realized exclusively via carbon atoms but via the hetero-atoms: oxygen, carbon and nitrogen and in view of the tremendous multitude of the polyoxy compounds alone, having a greater field of action than that which could be covered by the condensation processes or by the polymerization processes.

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After the research work of Carother in the field of superpolyamides had become known, there existed within the I.G. the most urgent problem to create something similar or something even superior, independent from the Dupont patents.

We therefore, for the time being, exclusively applied ourselves to the addition of diisocyanates to diamines and to glycols in order to produce in this manner high molecular linear polyureas or polyurethanes. In this connection it was found that one obtains with the use of long chain aliphatic diamines and aliphatic diisocyanates only unmeltable and strongly hydrophil polymers which cannot be worked in the melting ^{spinning} processes and therefore must be eliminated for the chemistry of plastics for all practical purposes. A basic polyurea produced in this manner is, however, technically used as animalizing agent for cuprammonium rayon.

POLYUREA.
Standard

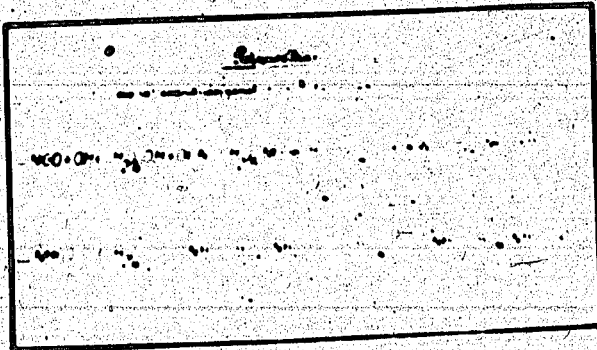
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from:

On the other hand the linear polyurethanes proved to be plastics which could be used in many fields possessing in part still more valuable properties than those possessed by the superpolyamides.

From the large number of linear polyurethanes used I want to mention here only a few characteristic ones. The product which is most ^{easily} accessible from a technical point of view is the polyurethane from 1.6-hexanediiocyanate + 1.4-Butylene-glycol.



It proved to be especially suitable for the production of rayon, plastics, and above all, of bristles. In technical operation it is produced by the addition of 1 mol of ^{very} pure 1.6 hexamethylenediiocyanate to 1 mol 1.4-Butyleneglycol in monochlorobenzene solution, in connection with which the addition or polymerization takes place under strong generation of heat (52 cal. per mol or 208 cal/kg polyurethane). After about 1 hour of reaction the polyurethane separates as a fine sandy powder in a practically quantitative yield.

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Depending on the reaction temperature and the remaining in the dissolved condition which one can adjust by the addition of dichlorobenzene, etc. or by breaking of the chain with mono-functional compounds, one is able to synthesize ^{in the presence of} the most varied polymerization degree.

The properties and differential characteristics of such a polyurethane which is placed on the market as Igamid U for plastics with a K-value of 60-70 and as Perlon U with a K-value of 55-60 in the form of rayon and bristles, as compared with Nylon and Perluran material, are the following:

On account of its ^{manner of} reaction, the polymerization in solvents and precipitation after having reached a certain degree of polymerization, the Igamid-U is more uniform as a polymer than the superpolyamides obtained by condensation. This, for instance, is expressed by the softening and melting points which are very close to each other.

Of all spinnable and linear superpolymers, important from an industrial point of view at the present time, Perlon-U has the lowest melting point which is approximately the same as that of acetate rayon which is undesirable for a number of textile uses.

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TRANSLATION

Specific Gravity
 Melting point
 Injection Molds
 Brinell Hardness
 Vicat Degree
 Impact resistance
 Pressed products
 (illegible)
 Tensile Strength
 Resistance to cold
 (illegible) Plastic
 Tensile Strength
 Elongation %
 Resistance to cold

PHYSICAL PROPERTIES OF IGAMIDS.

	Sample A	Sample B	Sample C
Specific Gravity	about 1.15	1.15	1.15
Melting point	at 195°	195°	200°
Injection Molds			
Brinell Hardness	110	1000	1000
Vicat Degree	170-180	180-190	180-190
Impact resistance	at 100	at 100	-
Pressed products (illegible)			
Tensile Strength	600	-	600
Resistance to cold (illegible) Plastic	+5°	-	+15°
Tensile Strength	1100	1100	1100
Elongation %	10	10	10
Resistance to cold	-30	-	-30

① - longitudes
 ② - curves

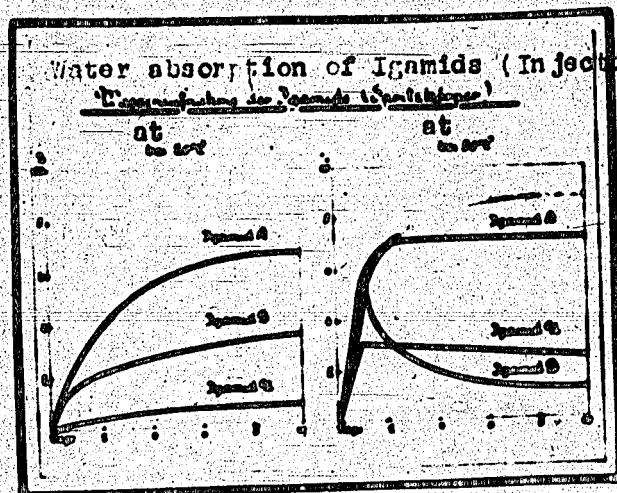
The tensile strength of rayons and bristles produced from polyurethanes are, for all practical purposes, equal to those of the superpolyamides. In the Laboratory it was possible to obtain with Perlon-11 peak tensile strength values up to 7.5 g/den (genuine silk 3.5 g/den). It is therefore also possible here to produce filaments (yarn) which greatly exceed the strength of the best genuine silk by more than 100%.

Especially characteristic for Igamid-U and all other polyurethanes is the fact that they absorb water to only a slight degree.

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from:

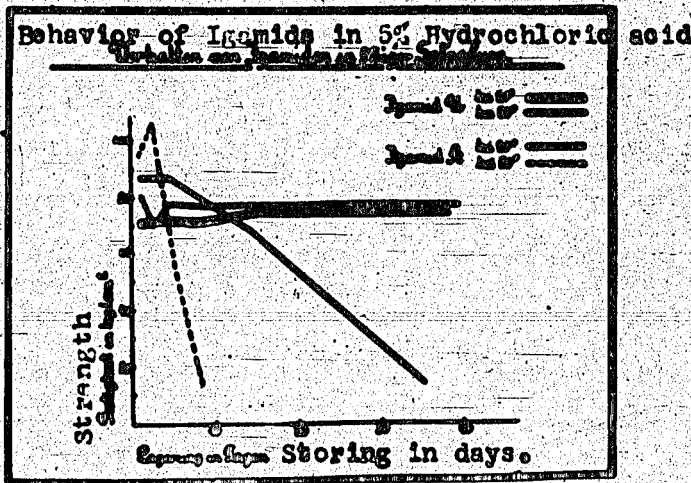


With increasing CH_2 number of members in the polyurethane chain it is true the water absorption property is still considerably reduced but at the same time - inasmuch as the molecule becomes gradually more and more paraffin-like, the tensile strength and also the melting points drop considerably.

The polyurethanes are superior to the polyamides also in connection with the electric properties and in the resistance to weather. They furthermore excel by an increased resistance to acids.

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from:



These special properties in combination with the other good properties of the superpolyamides make the Igamid-U a valuable high melting thermo-plastic material also in the field of plastics. The injection and extrusion products produced from same are insensitive to water and air moisture and above all they are accurate in size and gauge. All these properties will make it possible to introduce Igamid U or Perlon U into the technical field for a number of special uses, for instance for the manufacture of filter cloths fast to boiling and acids; acid and rust-resisting apparel, driving belts, rope, cable insulations, etc. In the textile field, for instance, the slight absorption of

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from:

water of the polyurethanes will prove to be disadvantageous for many purposes as for instance for underwear, while on the other hand it will prove to be advantageous for the manufacture of hydrophobic ladies hosiery.

Perlon U, on account of its hardness, its elasticity, which is similar to that of retail stockings, and its lack of sensitivity to moisture within a temperature range of up to $\sim 80^{\circ}$, is a valuable product for the manufacture of synthetic bristles and horsehair. Also in connection with dyeing, Perlon U differs from the superpolyamides; inasmuch as it does not contain any basic groups, it cannot be dyed like the latter with acid dyestuffs but only with acetate rayon or suspension dyestuffs. On account of the lack of basic groups, Igamid U also in the melted condition is considerably more insensitive to the air oxygen than the superpolyamides so that a browning of the material during the melting, extrusion (injection) and spinning will not occur even in case of incomplete exclusion of air.

In itself other physical phenomena and its further working, for instance in connection with its stretchability (elongation) to over 400% of its original length under orientation of the molecular chains; its ^(lasting) deformation under the action of boiling water and simultaneous strong tensioning (board setting) it is similar to a far-

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TRANSLATION

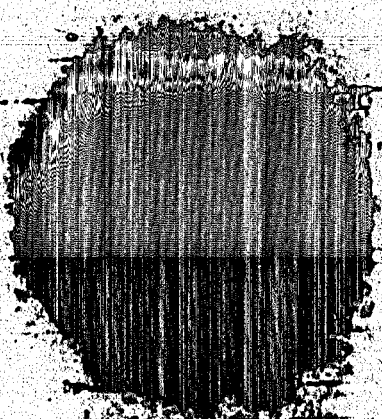
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reaching extent to the superpolyamides.

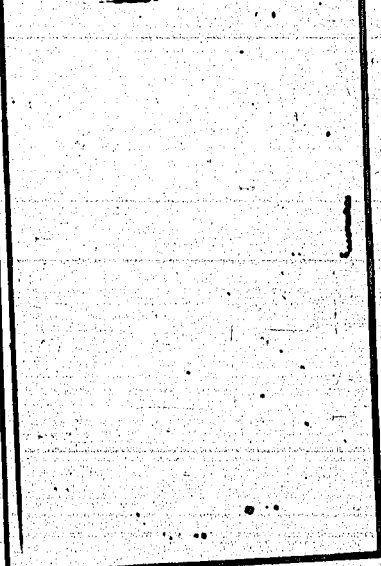
XRAY DIAGRAMS OF FOAMED

15.12.51



In unorientated condit
a) in unorientierten Zustand

STRETCHED IGAMID U CHAIN



In orientated condit
b) in orientierten Zustand

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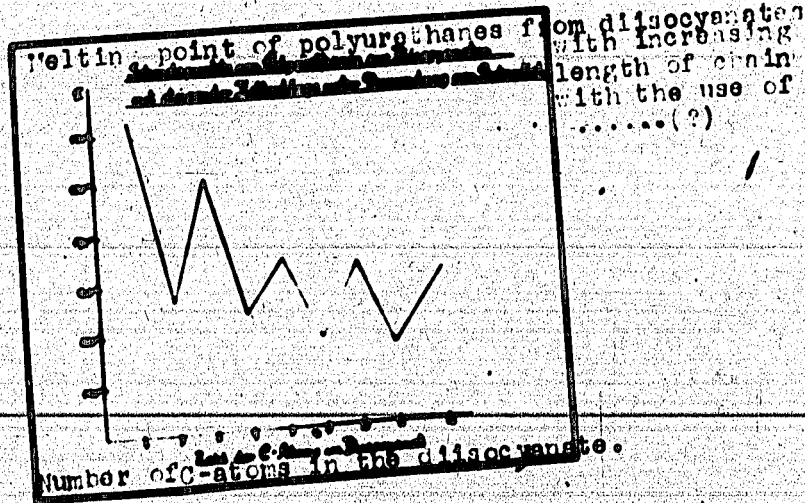
TRANSLATION

FROM:

Melting point of a few polyurethanes.

c - Number of members.

Temperature (Celsius)	99
0	103°
1	105°
10	111°
3	117°
8	123°
9	127°
12	133°

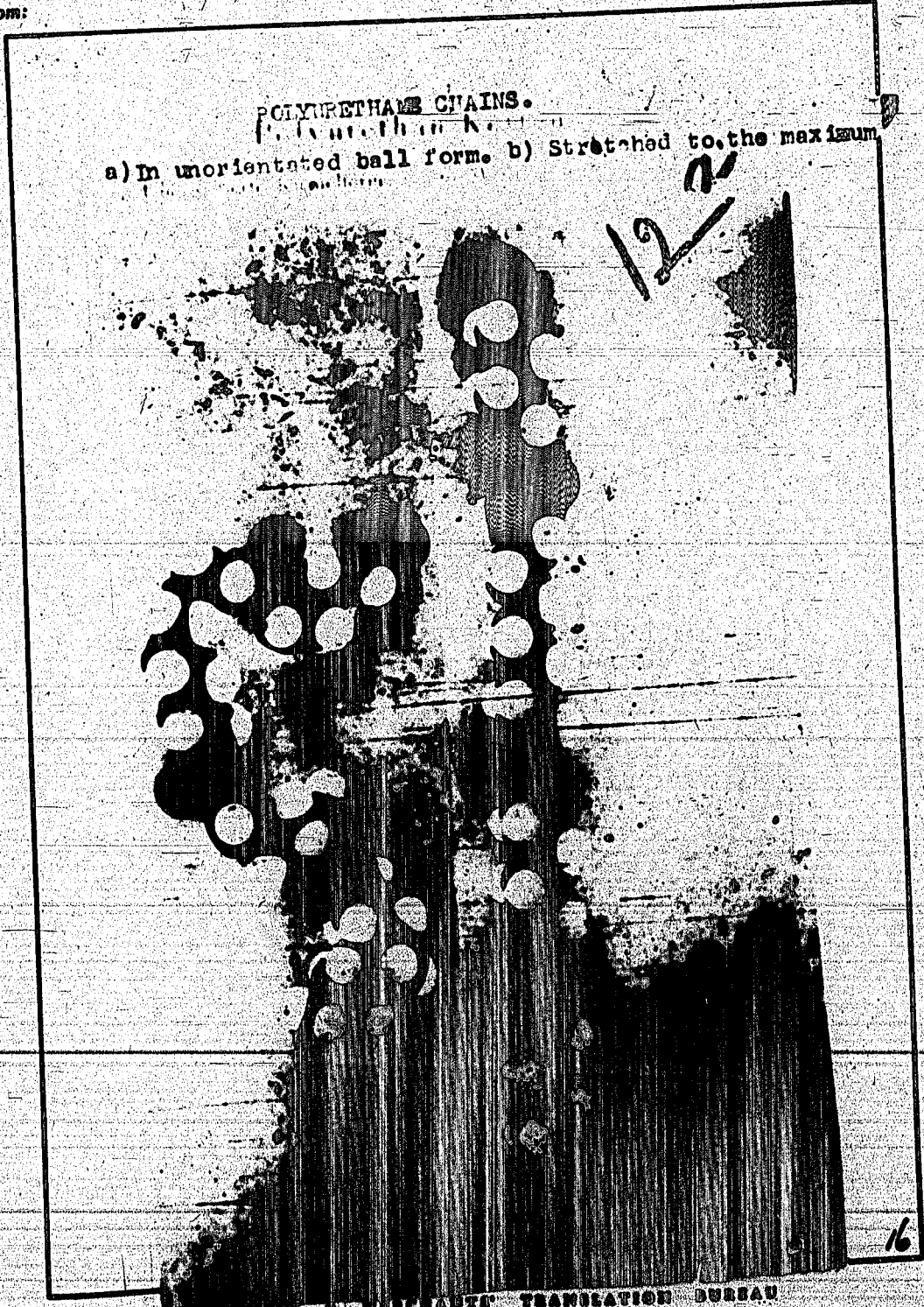


TRANSLATION

from:

POLYURETHANE CHAINS.

a) In unorientated ball form. b) Stretched to the maximum.



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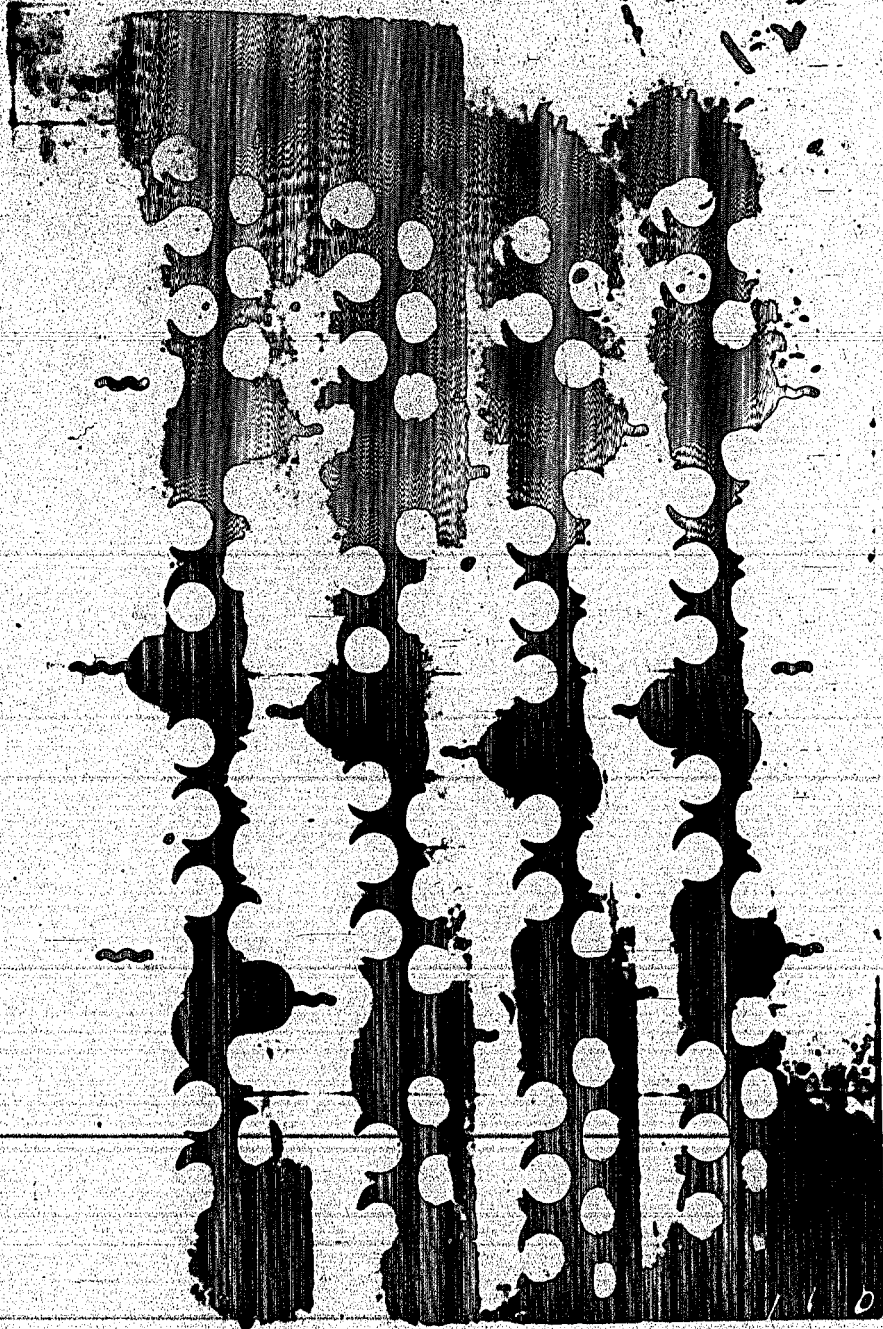
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POLYURETHANE CHAINS

100542



The original Polyurethane had been also
 25 mil or more Ketrolage als obiger Acetohalt
 The spinnable polyurethane molecule has a chain length which
 is about 25 times as great as that of the above section.

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from:

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In addition to this Igamid U or Perlon U, the following types will become of technical importance:

The polyurethane from the 1,4-Butane-diisocyanate + 1,4-Butylene glycol. It has practically the same properties as Igamid U. It melts, however, at a 12° C. higher temperature (melting point 194° C.). In all probability its cost price will also be lower than that of Igamid U and furthermore due to the total synthesis of the 1,4-Diaminebutane from acetylene and hydrocyanic acid it will make us independent of the phenol or benzol (benzene) basis.

As against these uniform polyurethanes which, in their low members, are completely insoluble in any solvents in the cold and are only soluble in a phenol - water mixture (90:10), we find that the mixed polyurethanes which are produced by a mixture of glycol- or diisocyanate-components are characterized by their good solubility in chlorohydrocarbons even in the cold, by a lower melting point and a greater thermo-plastic range, greater softness and greater tolerance to softening agents.

These are therefore the proper material for the manufacture of films, foils and leather substitutes.

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from:

An Igamid U, in which only 10 mol % of Butyleneglycol are substituted by Methyl-1.6-hexandiol, is considered more thermoplastic and on account of this is better suited for injection and extrusion molding than the uniform (1.6) material. It is furthermore important that it can be produced without any solvents simply by melting of the components together.

Generally it has been found immaterial in practice ^{what} glycols one should use for mixed polymerization in combination with the low-priced 1.4-butyleneglycol. As leather substitute Igamid UL, a mixed polyurethane, is contemplated for manufacturing purposes which is obtained by the melting together of 1 mol 1.6-Hexandisocyanate + 1/2 mol 1.4 Butyleneglycol + 1/2 mol methylhexandiol. A mixed polymerisate with very similar properties consists for instance of 1.2 mol 1.4- + 1/2 mol 1.6-diisocyanate and 0.8 mol 1.4-butyleneglycol + 0.2 mol methylhexandiol.

Igamid UL is a very soft ^{product} ~~substance~~ which easily dissolves in chloroform - alcohol mixtures. In many of its properties it is superior to harness leather.

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TRANSLATION

from:

PHYSICAL PROPERTIES OF IGAMIDS FOR LEATHER
SUBSTITUTE PURPOSES.

Physical Properties of Igamid for Leather Substitute

	Brand of Igamid	Brand of Leather	Remarks
Compressive strength	100	100	100
Tensile strength	100	100	100
Modulus of elasticity	100	100	100
Impact strength	100	100	100
Water absorption	100	100	100
Heat stability	100	100	100
Chemical stability	100	100	100
Resistance to abrasion	100	100	100
Resistance to staining	100	100	100

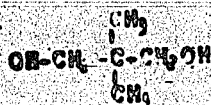
(Translator's Note: I have not been able to decipher the original as the photostat is not legible.)

None of the other Igamid brands, those which enter into question for leather substitute, has a somewhat higher L-strength and above all it has the advantage that it is practically insensitive to water and therefore does not show any longer

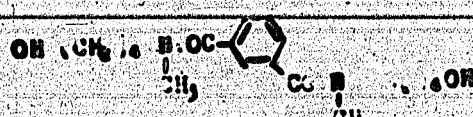
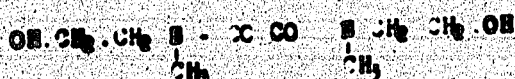
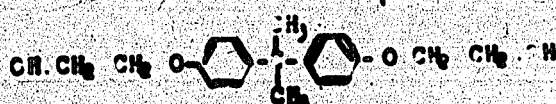
TRANSLATION

the tendency to break in case of extreme dryness or upon heating in water.

In view of its elastic properties the polyurethane of 1 mol 1,6-diisocyanate + 1/2 Mol 1,4-Butylene glycol + 1/2 Mol



is especially suitable for the impregnation and backing of fabrics. Other interesting polyurethane types which are still in the examination stages, are partly produced from the lower priced aromatic diisocyanates + aliphatic glycols or from aromatic glycols with hetero atoms, i.e.



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TRANSLATION

from

of from aliphatic linear polyesters with free hydroxyl groups, etc.

There are used as electrolyzing foils, sausage casing or skins fast to boiling, carriers or supports for photographic films and for (Translator's Note: Pages 16 and 17 are missing).....

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..... such lacquer solution is then sprayed on and then set aside at room temperature or baked in by heating to temperatures of up to 160° C. In this connection there is produced an absolutely insoluble and unmeltable lacquer coating, the elasticity and hardness of which one can adjust at will ^{by using} mainly aliphatically or mainly aromatic components.

An obvious condition for this manner of operation is, of course, that the reaction components do not react, at ordinary temperature, prematurely upon each other as otherwise the lacquer solutions swell up. This requirement is complied with in a satisfactory manner by a few diisocyanates. The freshly produced solutions are stable, depending on the conditions and the starting ^{products}, for many hours and even frequently for days.

It has furthermore been found especially when using organic cellulose derivatives that the stability can be increased by using certain stabilizers. Such stabilizers are, for instance, azo dyestuffs soluble in organic solvents and certain acid reacting compounds such as thiourea and its derivatives (Annotation J. 67 162).

Of the technically accessible (usable) diisocyanates the following enter into question for practical use arranged in accordance with their reactivity.

TRANSLATION

from:

1.) 1-Chlorophenyl-2,4-diisocyanate

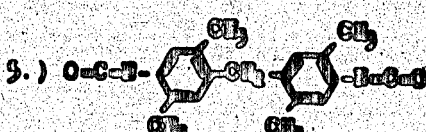
(referred to as
Diisocyanate)

2.) m-Toluyldiisocyanate

3.) 1,6-Hexamdiisocyanate

4.) Diisocyanate and Diamidic

Am
P.P. 125° (1/2 Mol. Diisocyanate)



Slowly Heating
(Diisocyanate)

P.P. 129°

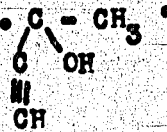
The question as to the stability of initial lacquer mixtures in accordance with the new process can also be contemplated from a basically different angle. As a matter of fact in the place of the diisocyanates one can also use compounds which react in the heat like diisocyanates i.e. which split off with the formation of diisocyanates. These are, for example, the bi-phenylurethanes corresponding to the

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from:

adduction products which split (dissociate) easily can be
produced from diisocyanates phenylmethylpyrazole, diphenyl-
amine or $\text{CH}_3 \cdot \text{C} \cdot \text{CH}_3$



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TRANSLATION

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These "dissociated diisocyanates" have the great advantage that their initial lacquer mixtures are stable for an unlimited period of time. As a matter of fact, one can even use solvents containing hydroxyl groups inasmuch as these solvents in most cases evaporate before a splitting back into diisocyanate occurs. However, in exchange for this, there is the disadvantage of a higher baking temperature and the frequently less remarkable fact that undesired split pieces occur. However, in case of larger tests, it was found that the occurring phenol or the generated malonic ester and its decomposition products also evaporate during the baking and have no further disturbing action. With these agents, it is true, one can push the reticulation more easily to a certain degree than with the use of free diisocyanates inasmuch as the completely reticulated polyurethanes by no means always represent the optimum.

From the tremendous number of polyoxy compounds which can be produced economically, the following have proven to be especially suitable:

- 1) A saponified mixed polymerisate from 80% vinyl chloride plus 20% vinyl acetate.
- 2) A hydroxyl group containing polyester, produced by vacuum esterification, from about 3 mols adipic acid or thiodipropionic acid, phthalic acid, etc. and 4 mols trimethylolpropane 1,2,4-trioxybutane, etc. by mixing the

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from:

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acid components, one is able to vary the elasticity within wide limits.

3) The luphenes.

4) Benzyl cellulose.

5) Condensation products from the ester glycols in accordance with 2 + xyloformaldehyde resins rich in oxygen.

Summarizing, it may be stated that the new lacquer coatings - on basis of thorough tests made by the Lacquer and Varnish Divisions of the Le and Lu - have the following advantages:

1) As compared with the alkyd lacquers, they can be "baked in" at considerably lower temperatures, partly even at ambient temperature, and therefore also enter into question for a varnishing (lacquer coating) - in a quality which was not possible up to the present time - of paper, textile materials, leather, wood, rubber goods, plastics, etc.

2) They have a variation scope in their properties which can frequently not be obtained by other lacquers.

3) They excel by an exceptional adherence strength to the base and by a very high luster and are, in most cases, also very resistant to cold. Their water resistance and pigment-bonding property, weather resistance and solvent stability are exceptional.

4) Inasmuch as the diisocyanate groups react with all movable hydrogen atoms which, as a matter of fact, bring

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about the electric conductivity, the diisocyanate lacquers have a high electric resistance (specific resistance 10^{15} - 10^{16} ohm x cm) and also a remarkably good creeping current strength which is of special importance for the manufacture of cable varnishes.

Drawbacks for the new lacquer process are the following:

- 1) The slight stability of the finished lacquer solutions. It is necessary to work them in one day.
- 2) The use of solvents free from hydroxyl groups and the complete exclusion of water.
- 3) The sometimes pungent odor of low molecular diisocyanates.

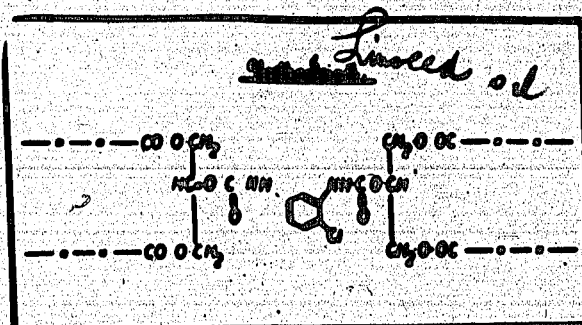
The good adherence property, the high elasticity and the resistance to boiling of some isocyanate lacquers make them appear especially suitable as coatings of deep drawing plates for cans for canned goods. Inasmuch as the reticulation takes place without the splitting-off of reaction particles, the lacquer coatings have furthermore a high imperviousness to gases. Remarkable for the diisocyanates for the lacquers is furthermore their high L₁ (mustard gas) resistance, which even exceeds considerably that of Oppanol. A paper impregnated with same (1 m² weighs 66 grams) with a lacquer application of only 14 g/m² has an L value of 13 St. (? hrs.) after MR 30 and of 4 hrs. after MR 50. The testing of these L-proof papers and fabrics is being carried out at

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the present time on a large scale.

Our ascertainment that the introduction of urethane groups imparts to the fabrics a high water resistance and that furthermore the molecular bond by means of diisocyanates represents an extremely mild structural principle, induced us to take up, on basis of these viewpoints, the very important and frequently taken up problem of improvement (ennoblement) of linseed oil.

We simply re-esterified with linseed oil with the computed quantity of glycerin or trimethylolethane into diglyceride and combined same by the addition of 1/2 mol chlorophenylene diisocyanate, into a molecule which only contains 4 drying fatty acid radicals.



In this way, depending on the degree of the re-esterification, one can produce oils of any desired viscosity which have not been subjected, like linseed oil-stand oil, 30

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and also certain alkydals, to the strong thermal operation of boiling to 280° C.

Linseed oil modified in this manner is considerably superior to the linseed oil-stand oil and furthermore, in the opinion of the Uerdinger Alkydal Division, has properties which are similar to those of the best Alkydal I extra, and furthermore, in addition to this, it has even the peak properties of all alkydals. As compared with Alkydal I extra, it has, among other things, the advantage of more rapid drying-on and thorough drying, of higher elasticity of the film, of a more rapid obtaining of the resistance to water, of higher compatibility with basic pigments and the fact that it does not subsequently thicken same.

Its only drawback is its somewhat slighter fastness to light.

oil types	Alkydal	Alkydal	Alkydal
best linseed oil	100	100	100
stand oil	100	100	100
modified linseed oil	100	100	100
stand oil	100	100	100
modified linseed oil	100	100	100
stand oil	100	100	100

As soon as large quantities of linseed oil are again available, Uerdinger will take up the manufacture of urethane linseed oil on a large scale, the cost price of which will

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from:

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be about equal to that of Alkyd I extra.

With these diisocyanate linseed oils, we have furthermore a number of further interesting possibilities of application in the field of rust protection, the manufacture of oil-silk, electro-insulating varnishes, putty masses for airplane construction, etc. and it is even possible to convert in the same manner poor drying oils such as train oil and sardine oil into rapidly and thoroughly drying oils (Application: J. 67 805 and J. 68 374).

For the manufacture of novel compression molding masses, one mixes the diisocyanate with the polyoxy compound approximately in a molecular ratio of the reactive groups and furthermore adds large quantities of filler, for instance sawdust, etc. and causes the addition of both components under pressure and heats in a manner similar to the manufacture of bakelite and urea molding materials (plastics). The drawback here, too, is the limited stability of the diisocyanate-polyalcohol mixture. In case of a careless working, they react already on the cylinder during the mixing of same. One can therefore depend for all practical purposes only on the use of the slowly-reacting and high-melting diisocyanates from dianisidine and from Di-p-xylylidimethane, with which one can obtain quite worthwhile results in combination with, *for example,* a polyester rich in hydroxyl groups, of adipic acid and trimethylolethane, of the kind similar to the one used for

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initial lacquer mixtures. In case of compression temperatures of about 140°-160° and a pressing time of 5-10 min., one obtains from same molded products which, at higher temperature, it is true, are still somewhat more thermo-plastic than hardened-out phenoplasts but which, on the other hand, are superior to same in essential properties. Their main advantages are the following:

- 1) A very high resistance to alkalis.
- 2) High electric resistance of about 3-5 Mill. Megohms as compared with 20,000 megohms in the case of bakelite.
- 3) High creeping current strength also in wet condition.
- 4) Essentially easier flowability than bakelite masses which, in accordance with the statement of Troisdorf, will make possible the production of molded (plastic) products of up to 3 times the weight of the phenol-formaldehyde molded articles which could be produced up to the present time.

Temperature of Molding (°C)	Weight of Molded Product (g)	Weight of Starting Material (g)	Volume of Molded Product (cm³)	Volume of Starting Material (cm³)	Ratio Molded Product to Starting Material
140	100	100	100	100	1.00
150	150	100	150	100	1.50
160	200	100	200	100	2.00
170	250	100	250	100	2.50
180	300	100	300	100	3.00
190	350	100	350	100	3.50
200	400	100	400	100	4.00
210	450	100	450	100	4.50
220	500	100	500	100	5.00

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5) The most important property of the new materials, however, is their high elasticity, which is expressed by their increased impact bending strength. In this way, the important problem of the creation of the so-called "elastic bakelite" has therefore ^{probably} been solved. In a manner similar to the field of lacquers, there is also here the possibility of producing by the use of mainly aliphatic components, soft and highly elastic materials and with the use of mainly aromatic starting materials, harder and more brittle plastic products. Even a considerable simplification of the heat-pressure manufacturing process appears possible: it consists, similar to the baking of porcelain, therein that the compression mixtures are molded in the cold and thereupon "baked out" without pressure in the oven. The reticulation takes place so quickly that no deformation or change in size takes place. (Application J 69 444.)

Such strongly reticulated polyurethanes will be used at the present time mainly for the manufacture of supporting structural parts for airplanes and the manufacture of certain large special bodies, in connection with which metal cannot be used and bakelite is not sufficient in view of a slight strength and brittleness. Also in the field of telecommunication technique, new interesting application possibilities will result. Inasmuch as the new plastic masses likewise have an excellent adhering strength to the materials

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covering them, they are, in accordance with the findings of Troisdorf, among many other purposes, excellent for the manufacture of high-grade grinding wheels, which is a large and important field of application, in which field at the present time the Bakelite Company still has the monopoly with its formaldehyde plastics with the addition of furfural derivatives.

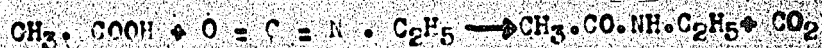
From among the large number of polyoxy compounds which are available at low prices, we have also examined into the reticulation of Cellit in a more thorough manner, which can be worked with diisocyanates likewise into non-melting molded articles which come out from the mold hot. Also here, an important field of application can be opened up for these products.

At this place, it may be mentioned that with the assistance of diisocyanates, one can also produce insoluble and non-meltable acetate rayon. Inasmuch as Cellit is spun from alcohol-acetone solution, one advisedly starts from the splitting agents already mentioned in connection with the lacquers which, upon heating of the thread (yarn) to about 130°C , are converted into the diisocyanates and thereupon completely reticulate the long cellulose chains. The process at the present time is being finally tested by the Aceta, with which the experiments are being carried out jointly. (Application J.67 163).

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In addition to the reactive hydrogen atoms of the hydroxyl and amino groups, the isocyanate group also reacts, as had also been ascertained by Wurtz as early as the year 1848, with the carboxyl group, for instance



in connection with which the acid amide is produced with the splitting-off of carbon dioxide. This reaction can be utilized for the production of novel and highly-resistant foam products. If one, for instance, combines a polyester of a dicarboxylic acid + a 3-valent alcohol, which still contains free hydroxyl groups and also carboxyl groups, with a diisocyanate, then there occurs already in the honey-like mass at 50° C, a reaction with the production of urethane and carbon amide bridges, with simultaneous splitting-off of carbon dioxide. In this way, the tough mass has risen like cake dough and hardens gradually more and more with further increasing reticulation. In this way, one is able to produce foam materials with very high strength and in any desired degree of elasticity. A material which, for instance, has a compressive strength (resistance to pressure) of about 10 kg/cm² with a sufficient heat resistance of up to 100° C is produced from toluenediisocyanate + a polyester of oxalic acid, adipic acid and trimethylolthane - specific gravity below 0.1. (Application J. 69 394).

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obtain temperature-resistant adhesions of standard buna-sulfur mixtures on iron, light metals, porcelain, etc. with strength figures of up to 80 kg/cm² (in other words, buna tears in itself and not at the place of adhesion). In this connection, we have found especially suitable the diisocyanates of the m-toluylenediamine and of the hexamethylenediamine, which are already available in the market under the name of Vulkollan T or H. Simply with their aid is it, for instance, possible today, without the use of natural rubber, to produce also cushions of tanks and the like - i.e. cementing of rubberized products. In Leverkusen, very intensive research work is being carried out in connection with the problem of producing, with the aid of these Vulkollans, a tire of metal cord threads and rubber which, up to the present time, was not possible on account of the insufficient adhesion between the rubber and the metal. If the solution of this important problem were found, then, in this way, there would be produced the high-heat-resistant tires which, above all, can be re-treaded any number of times, for instance, for low-priced cars.

The good adhesion property of buna-diisocyanate mixtures also makes possible the production of a new structural material for airplanes suggested by the Gothaer Waggonfabrik which consists of a welded thin plate of vulcan fiber and a sheet of light metal. The cementing thus produced tears more easily in the vulcan fiber or in the metal than at the

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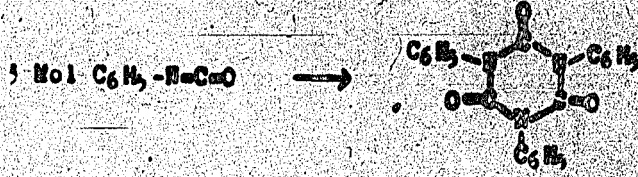
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place of adhesion (cementing). This material which therefore consists of light metal on the outside and of cellulose on the inside, makes it possible to produce a metal airplane in accordance with the structural methods used for wooden construction. In this way, it would be possible to save in connection with the building of a heavy bombing plane, about $2/3$ of the working hours required up to the present time. At the same time, the new material has a higher resistance to penetration than the light metal sheets without base. After the war, this construction material will also be used for the manufacture of bodies. From vulcan fiber with buna coating, there can also be produced an interesting material which is to be used for the manufacture of trunks for the Tropics.

The buna-isocyanate cementing will also find a further important field of application in connection with the novel buna spring constructions.

This success in the field of buna cementing, of course, induced the carrying on of experiments in order to test the diisocyanates in a very general manner also as to their suitability as cements. In this connection, it was found that with the aid of same, cementing or pasting problems which, up to the present time were considered insolvable, would be solved. Thus, for instance, it is possible to cement in the cold Oppanol skins with iron or wood, with

easily converted into the corresponding trimeric product.



With the aid of the diisocyanates, we were also able to solve the problem of the manufacture of an animalizing agent for cuprammonium rayon. On basis of thorough preliminary work, we have arrived at the knowledge that an animalizing agent which makes it possible to dye cellulose fibers by means of acid dyestuffs in the same shades as in the case of wool, must have the following properties:

- 1) Very high molecular size with already pronounced absorption property.
- 2) The basic nitrogen ^{responsible} ~~responsible~~ for the acid-combining property must not amount to about 3% ^{more than} in the molecule.
- 3) Complete insolubility of all salts, ^{also} in boiling water.
- 4) Complete colorlessness. Upon exposure to light, no browning must occur and the fastness to light of the acid dyestuffs must not be detrimentally influenced.
- 5) The animalizing agent must be present in the finest possible distribution.

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We thereupon worked out a pigment which consists of a basic polyurea, which is produced by a mixture addition of chlorophenylene diisocyanate + -Di(amidopropyl)-methylamine + any desired diamines (Application J. 64 249).

(It) our persistol salt (A-zirconium oxychloride) + persistol base B (paraffin emulsion) or with the single bath product Persistol N produced from both, there is obtained on textile materials a remarkably good laundry-proof water-repellent finish. However, it is not possible in this manner to produce ^{also} hydrophobic effect fast to dry cleaning with gasoline.

The diisocyanates afforded us the possibility of producing hydrophobic and at the same time gasoline-insoluble waxes. A satisfactory laundry-proof ^{gasoline fast} persistol base which is now being prepared and which is applied with zirconium oxychloride and a slight quantity of kaunit, contains a wax which is produced from 1 mol 1,6-hexandiisocyanate + 2 mols of a mixture of higher aliphatic alcohols (C₁₂-C₁₈) (J. 66 271, J. 68 279, J. 70 125.)

The starting materials required for the production of polyurethanes are diamine, phosgene, glycols and polyoxy compounds.

For the production of the linear polyurethanes, there are used, first of all, 1,4-Butyleneglycol and methyl-1,6-hexanediol. 1,4-Butanediol is now available, in accordance

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with the Peppe-Synthesis, from formaldehyde and acetylene at a very low cost and can be produced in industrial operation. The methylhexanediol is produced by hydrogenation of a mixture of the ester from raw methyladipic acid, as obtained in Leuna in connection with the oxidation of the cyclohexanol-methylhexanol mixture. The dimethyl-1,3-propanediol can also easily be obtained from isobutylaldehyde + formaldehyde and subsequent hydrogenation also on an industrial scale. The introduction of further methyl groups or of large side chains results in linear polymers, the strength properties and melting points of which already drop greatly.

The starting materials for the diisocyanates are the corresponding aliphatic and aromatic diamines which are converted with phosgene into the diisocyanate



Of the aliphatic straight chain diamines, the 1,6-hexamethylene-diamine can be obtained, in accordance with the known process, by the hydrogenation of adipic acid dinitrile. However, we are trying to start with the 1,4-diaminobutane, inasmuch as one can produce ^{more} economically from acetylene and HCN,

and therefore independently of the phenol and benzene basis.

As a matter of fact, we have found that one can produce nitrile directly from acetylene and hydrocyanic acid by means of cupric chloride catalysts, at a low price, and that it

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that we shall enter the free base into dichlorobenzene phosgene, in connection with which, in all probability, first of all the hydrochloric acid salt of the aminocarboxylic acid chloride will be produced, namely:



which can be further phosgenized without any difficulties. The production of pure diisocyanates which, as a matter of fact, are very sensitive products which polymerize easily, caused great difficulties at the beginning.

The conversion of aromatic diamines into diisocyanates is always very easy. The lower members can still be distilled while the diisocyanates with 2 benzene nuclei can no longer be distilled on a large scale, but separate in some cases practically quantitatively from the chlorobenzene after phosgenizing.

As already mentioned, the linear polyurethanes will have approximately the same cost price as the polyamides; in connection with the polyurethane leather which is produced in the melt, we believe that we shall even be able to obtain cost prices which are lower than the competing polyamide brands. The cost prices of the aromatic diisocyanates will be between RM 1.80 and 2.30, so that for the manufacture of high-class lacquers (varnishes or coatings) and compression-masses, of which only a fraction consists of the diisocyanates, the cost prices will be very satisfactory.

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I have now explained to you in outline the new and far-reaching application possibilities of the diisocyanates. Therefore, if we applied today for the issuance of a permit for a manufacturing plant for the manufacture, for the time being, of 200 Moto aliphatic and 100 Moto aromatic diisocyanates, this first enterprise is probably justified on account of the surprisingly many-fold fields of application and also for the reason that after the war they will fill a real need.