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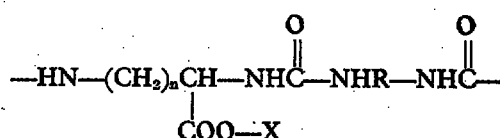
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COMPLETE SPECIFICATION

Polyureas and their production

We, MERCK & Co. INC., a corporation duly organised and existing under the laws of the State of New Jersey, United States of America, of Rahway, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

- 10 This invention is concerned with novel polyureas and methods for producing them. Each polyurea of this invention consists essentially of a plurality of units which recur and each of which is within the following generic Formula I:

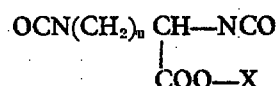


- in which X in each of the recurring units is a hydrogen atom, an alkali metal atom, preferably sodium, potassium or lithium, or an alkyl radical of formula $\text{—CH}_2\text{—R}_1$ where R_1 is hydrogen or an alkyl radical of 1—21 carbon atoms; n in each of the recurring units is 3 or 4; R in each of the recurring units is divalent a hydrocarbon radical of 2—10 carbon atoms, either unsubstituted or carboalkoxy-substituted, e.g. is alkylene or alkylidene, phenylene, ($\text{C}_6\text{H}_4\text{=}$) or an alkyl substituted divalent mononuclear aryl such as $\text{CH}_3\text{—C}_6\text{H}_3\text{=}$ or a mononuclear aralkylene such as $\text{C}_6\text{H}_{10}\text{—(CH}_2\text{—)}_2\text{—}$.



- a divalent cycloalkyl radical such as $(\text{—C}_6\text{H}_{10}\text{—})$ or a cycloalkyl alkylene radical such as $\text{C}_6\text{H}_{10}\text{—(CH}_2\text{—)}_2\text{—}$.
- 35 Those polyureas of Formula I in which X
- [Price 4s. 6d.]

is alkyl are produced by reacting one or more diisocyanate alkylesters of the generic formula A:



where X is an alkyl radical of 1—22 carbon atoms and n is 3 or 4 with one or more diamines of the generic formula B:



wherein R is as before defined. When X is alkyl the polyureas of Formula I are usually high-melting and are further characterized by having the unexpected property of being more flexible than the corresponding polyureas derived from the conventional aromatic diisocyanates such as the toluene diisocyanates. The polyureas which X is alkyl may be reacted with an appropriate alkali metal compound in aqueous solution to hydrolyse some or substantially all of the ester groups. This may be effected in one of two ways: the first involves a two phase reaction of the polyurea suspended in a 10% aqueous solution of sodium carbonate, for example, which is heated and maintained at 50°—95°C to effect hydrolysis. The second involves solution of the polyurea in dimethyl sulphoxide followed by the addition of dilute aqueous sodium hydroxide while maintaining the pH below 10.0 by slow dropwise addition. By following either of these two methods hydrolysis is substantially complete in one hour resulting in the production of a water-soluble polyurea sodium salt within the generic formula I in which X is sodium. Addition of 10% hydrochloric acid to a thrice water-diluted reaction mixture of the sodio-polyureas causes the replacement of sodium by hydrogen and results in the precipitation of the polyurea in which X is

hydrogen. This precipitate is redissolved in dilute alkali and reprecipitated as before with hydrochloric acid. By controlling the proportion of alkali metal reactant the degree of replacement by sodium of the alkyl radicals in the individual polyureas may be controlled. If desired the quantity of HCl added may also be controlled so that only some of the sodium atoms are replaced by hydrogen in the individual units of the polyureas. Thus by controlling the quantity of alkali metal reactant and/or the quantity of acid addition there may be obtained a wide variety of different polyureas of significantly different properties making them useful in a number of different fields: they are polyureas of Formula I in which X in some of the recurring units is an alkali metal (preferably Na, K or Li), and in others is an alkyl radical; they are polyureas of Formula I in which X in some of the recurring units is hydrogen and in others is an alkyl radical; they are polyureas of Formula I in which X in some of the recurring units is an alkali metal and in others is hydrogen; they are polyureas of Formula I in which X in some of the recurring units is hydrogen, in other units is an alkyl radical and in still other units is an alkali metal.

Those polyureas in which X is an alkali metal are useful as soil suspension agents. For example, a suspension of activated carbon in water settled to the half way mark in 80 seconds. It has been found that the addition of a very small proportion of said sodio-polyureas held the carbon in suspension above the 50% volume line, for considerably longer periods of time measured in hours. The novel polyureas in which X is hydrogen in at least some of the recurring units provide sites of ionic attachment of basic dyes. Even those in which the carboxylic acid groups are only partially hydrolysed provide the free acid groups (—COOH) as sites of such ionic attachment for basic dyes. The polyureas of this invention have increased dyeability and are alloyable with other polymers for imparting this property to the polymer combination.

The polyureas of Formula I in which X is an alkyl radical may be deposited from dimethyl sulphoxide solution to form clear, tough, pliable films on glass. The generic method for producing these novel polyureas is either by interfacial or solution polymerization. In the interfacial method it is preferred to use a low-

boiling halogenated hydrocarbon such as methylene dichloride, chloroform, carbon tetrachloride or a polyhalogenated ethane to dissolve a diisocyanate reactant of Formula A. The diamine of Formula B is dissolved in water. These two solutions are admixed with each other under efficient high speed stirring conditions whereupon the polyurea so formed precipitates out. The raw polyurea precipitate is filtered, washed free of unreacted starting materials and solvents and is then vacuum dried.

An alternative method of synthesis is by reaction of compounds of Formula A with compounds of Formula B in a non-protonic solvent. Although dioxane, ethylene glycol ethers and dimethyl formamide are useful solvents in this reaction, dimethyl sulphoxide is preferred. A dimethyl sulphoxide solution of the diisocyanate solution of Formula A is poured into an amine solution with the same solvent while maintaining the temperature of the mass below 50°C with good stirring and the use of a water bath cooler. The reaction is compelled in most cases by subsequently heating to and maintaining the mass at $60^{\circ}\text{—}80^{\circ}\text{C}$ for several hours. The resultant polyurea obtained is isolated by pouring the mass into 2—4 times its volume of a non-solvent such as acetone or water. After stirring for several hours with several changes of non-solvent, the dimethyl sulphoxide is leached away and the thick liquid becomes solid. The solid is dried in vacuo at $60^{\circ}\text{—}100^{\circ}\text{C}$ to remove last traces of the sulfoxide.

Reduced viscosities of said novel polyurea esters are run either in dimethyl sulphoxide or in formic acid at 1% concentration of polyurea. The softening and melting points are taken on a Kofler Hot Bench. The melting point is the temperature at which a liquid smear appears on the hot surface when the polyurea is pressed and stroked with a hot spatula.

The following Table I shows some of the physical properties of various polyureas of this invention and namely such polyurea esters within generic Formula I in which X is CH_3 , and R is the divalent hydrocarbon radical of the particular amine: the said polyureas were produced by the methods as indicated in the table with 1 mole of lysine diisocyanate methyl ester reacted with 1 mole of the respective amine set forth in the table:

TABLE I

Polyurea Esters

Diamine	Reaction Type	Reduced Viscosity	Viscosity Solvent	Softening Point °C.	Melting Point °C.
Ethylene Diamine	1	0.33	DMSO	157	167
1,3-Propane Diamine	1.	1.32	DMSO	140	170
1,6-Hexane Diamine	2.	0.267	DMSO	142	150
1,4-Bis (Aminomethyl) Cyclohexane	2	0.936	HCOOH	184	200
m-Phenylene Diamine	2	0.225	HCOOH	175	190

1. Homogeneous solution in dimethyl sulphoxide (DMSO).

2. Interfacial polymerization $\text{MeCl}_2\text{—H}_2\text{O}$.

The following Table II shows some of the physical properties of various polyureas of this invention and namely some polyurea free acids within generic Formula I but wherein X is hydrogen, R is the divalent hydrocarbon radical of the particular amine, and n is 4. 5

TABLE II

Polyurea Acids

Diamine	Reduced Viscosity	Viscosity Solvent	Softening Point °C.	Melting Point °C.	Acid Equivalent	
					Found	Calculated
Ethylene Diamine	0.30	DMSO	150	173	257.0	258.0
1,6-Hexane Diamine	0.126	DMSO	140	153	404.5	314.4
m-Phenylene Diamine	0.155	HCOOH	220	232	455	306

10 In general the reactants of Formula A are prepared by reacting a dihydrochloride of C_{1-22} alkyl esters of ornithine or lysine with phosgene. Such reaction is carried out in the presence of a suitable solvent which is inert with respect to the reactants employed under the reaction conditions used. Examples of some of such solvent are chlorobenzene, orthodichlorobenzene, the bromotoluenes and chlorotoluenes, benzene, toluene, dioxane, 4-chloro-1,3-xylene and dialkyl ethers of glycols and polyether glycols. The temperature at which the reaction is carried out is in the range of 50°—200°C although the particular temperatures employed will be dependent upon the particular esters used as reactants.

25 In the following examples, in which the word 'Dowex' is a trade mark, some of the specific compounds within generic Formula A and methods for making them are illustrated.

EXAMPLE A—1.

Lysine Diisocyanate Methyl Ester.

250 g. of lysine monohydrochloride suspended in 2500 ml. of absolute methanol is dissolved by passing into the stirred suspension dry hydrogen chloride. The reaction temperature immediately goes up to 47°C and in 10 minutes all the solids are dissolved. The gas is passed in for five minutes longer. The reaction mass is then permitted to cool slowly to room temperature with stirring. Crystals start to form in 2.5 hours. The reaction mass is stirred for a period of 15 hours at a temperature of 25°C. The product is precipitated by adding 1.5 liters of diethyl ether over a period of 15 minutes. After one hour of stirring, the product is isolated by filtration and washing with 3 parts of ether dissolved in two parts of methanol, followed by a diethyl ether wash. The product lysine dihydro-

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chloride methyl ester is dried to constant weight at 65°C in a vacuum oven.

The lysine methyl ester dihydrochloride is finely ground in a mortar and 186 grams is suspended in 2100 ml. of freshly dried and redistilled *o*-dichlorobenzene in a 3-neck flask.

Phosgene is passed into the reaction vessel at a rapid rate while raising the temperature of the suspension to 150–155°C. As the reaction proceeds the solution becomes clearer and darker. Hydrogen chloride evolution is indicated by fuming from the condenser as it hits the moist atmosphere. After twelve hours, no more hydrogen chloride evolves. Phosgene is passed in for one more hour and nitrogen is then bubbled through the reaction vessel as the solution temperature drops to 25°C, to remove residual phosgene and hydrogen chloride. The remaining solids are removed by filtration and washed. The filtrate is then distilled and under reduced pressure. The solvent, *o*-dichlorobenzene, is distilled at 44°C and 2 mm. pressure. The product lysine diisocyanate methyl ester, is distilled at 123°C, at 0.45 mm. pressure. A clear, colourless liquid product is obtained having a refractive index of 1.4565 at 24.5°C.

In an analogous manner, the lysine diisocyanate ethyl, propyl, butyl or pentyl esters are prepared by substituting equivalent amounts of ethanol, propanol, butanol or pentanol for methanol in the foregoing procedure.

EXAMPLE A—2.

35 Lysine Diisocyanate Octyl Ester.

18.2 g. (0.1 mol) of L-lysine monohydrochloride is suspended in 140 ml. of *n*-octanol containing 0.24 moles of *p*-toluenesulphonic acid. The mixture is heated until water and octanol begin to distil and the reaction temperature is then maintained at 120–130°C. by addition of *n*-octanol. After 240 ml. of *n*-octanol has been added and removed over a two hour period, the residual alcohol is removed by vacuum stripping. The waxy reaction product, the di-*p*-toluene sulphonate salt of lysine *n*-octyl ester, is recrystallized from a mixture of ethanol and ether.

A solution of 73 grams of this waxy product in 150 ml. methanol is adsorbed on a column of 500 ml. of a strongly basic styrene-divinylbenzene anion-exchange resin (Dowex 1—X8) which had previously been activated on the hydroxyl cycle with aqueous ammonia, washed to neutrality, and had its water displaced with methanol. The product is eluted from the column with methanol. The free base ester is not isolated but converted to the dihydrochloride by addition of anhydrous HCl and the dihydrochloride recovered by precipitation with diethyl ether. The dihydrochloride is suspended in 275 ml. of toluene and 0.45 moles of phosgene added at 60–70°C. When evolution of HCl ceases, the temperature of the reaction mass is gradually increased to strip

out the solvent. The product, lysine diisocyanate *n*-octyl ester is recovered by vacuum fractionation, b.p. 137–142°C. at 0.2 mm.

When the foregoing procedure is repeated using equivalent amounts of hexanol, decanol, dodecanol, or tetradecanol in place of octanol, the corresponding hexyl, decyl, dodecyl, or tetradecyl ester of lysine diisocyanate is obtained.

EXAMPLE A—3.

Ornithine Diisocyanate Hexyl Ester.

A suspension of 16.8 grams (0.1 mole) of L-ornithine monohydrochloride in 100 ml. of *n*-hexyl alcohol containing 45.6 grams of *p*-toluenesulphonic acid monohydrate was heated to 110°C for reaction while water and some hexanol were removed. Hexanol was added to replace that lost from the reaction mixture. After water evolution ceased the excess of hexanol was removed by vacuum stripping and the residue recrystallized once from ethanol-diethyl ether. Without further purification, methathesis was effected over a "Dowex 1—X8" column in the general manner set forth in Example A—2 herein. The effluent was neutralized with HCl and the resultant L-ornithine hexyl ester dihydrochloride was recovered by precipitation with diethyl ether. The dihydrochloride as treated in the manner set forth in Example A—2 whereby ornithine diisocyanate hexyl ester was recovered.

When the foregoing procedure is repeated using equivalent amounts of other alkanols such as butanol, octanol, decanol, dodecanol or tetradecanol in place of hexanol the corresponding butyl, octyl, decyl, dodecyl, or tetradecyl ester of ornithine diisocyanate is obtained.

EXAMPLE A—4.

L-Lysine Butyl Ester Diisocyanate.

To a suspension of 18.2 grams (0.1 mole) of L-lysine monohydrochloride in 80 ml. of *n*-butanol was added 0.24 moles of *p*-toluene sulphonic acid. The mixture was heated until water and butanol distilled and then addition of *n*-butanol began to maintain a constant reactor volume. After 240 ml. of *n*-butanol had been added and removed over a two-hour period, the residual butanol was removed by vacuum stripping. The oily residue was recrystallized from ethanol-diethyl ether to yield 88% of product, m.p. 146–148°C. Analyses were satisfactory for $C_{24}H_{44}N_2S_2O_8$.

Calc.: 52.7% C, 7.0% H, 11.7% S
Found.: 52.5% C, 6.9% H, 11.4% S

A second crop was recovered to make the overall yield 95%.

This product was converted into the corresponding dihydrochloride by use of an ion exchange resin to produce the free ester and then by treatment with HCl. The dihydrochloride was reacted with phosgene in the

manner described in Example A—2 to obtain the diisocyanate ester.

EXAMPLE A—5.

L-Lysine Stearyl Ester Di-p-Toluenesulfonate & Diisocyanate.

- A mixture of 18.2 grams lysine monohydrochloride, 45.6 grams of *p*-toluene sulphonic acid hydrate and 270 grams of stearyl alcohol was heated at 125—128°C for 2 hours. The product was washed well with ether to remove the excess of alcohol and recrystallized from a mixture of methanol-ether. In spite of a relatively high m.p. range, 161—199°C., the sample analysed correctly for $C_{36}H_{66}N_2S_2O_8$ —
- 15 Calc.: 61.4% C, 8.9% H, 3.8% N
 Found: 61.7% C, 8.7% H, 3.9% N
- This product was converted to its hydrochloride salt and precipitated out with ether, and finally reacted with phosgene all in the manner of Example A—2 thereby to produce its diisocyanate which was recovered.

EXAMPLE A—6.

L-Lysine-Decyl Ester Dihydrochloride and its Diisocyanate.

- 25 25 grams of L-lysine ether ester dihydro-

chloride, melting point 145°C., was suspended in 200 cc. of Enjay decyl alcohol, a mixture of 10-carbon primary alcohols chosen because it was cheaper than *n*-decyl alcohol. The suspension was heated to and maintained at 110°—115°C while anhydrous HCl was passed in. A clear solution was obtained in about one hour. Then mild vacuum was applied with continued HCl sparging until 40 cc. of alcohol-water were removed. The mixture was allowed to cool to 25°C. and HCl sparging was discontinued. Then 250 cc. of anhydrous ether was added thereto and the L-lysine decyl ester dihydrochloride precipitated out as a gum which was washed with ether as in the first example.

Then to the gummy mass was added 250 cc. of toluene and the mixture was phosgenated at 65°—70°C. for 5½ hours until no more HCl evolved. Only trace amounts of solids were present. The mixture was fractionated as follows:

Cut #1	B.P. 102°C. 4.5 mm.	1.4 grams $n_D^{25} = 1.4409$	
			$\begin{array}{c} \text{O} \\ \parallel \\ \text{O}-\text{C}-\text{Cl} \end{array}$ I.R.: mostly $\text{O}-\text{C}-\text{Cl}$ and small amount of NCO Found Cl—12.95%
Cut #2	B.P. 95—105°C. 0.060 mm.	2.7 grams $n_D^{25} = 1.4529$	
			I.R.: mostly L-lysine ethyl ester diisocyanate Found Cl—1.07%
Cut #3	B.P. 120—135°C. 0.080 mm.	2.6 grams $n_D^{25} = 1.4565$	
			I.R.: similar to cut e4 but small amount of L-lysine ethyl ester diisocyanate impurity
Cut #4	B.P. 135—145°C. 0.080 mm.	2.9 grams $n_D^{25} = 1.4591$, water white	
			Found C= 63.78, H=8.46, N=8.97, Cl=0.25 Calculated for $C_{18}H_{30}N_2O_4$ — C=63.88, H=8.97, N=8.28
Cut #5	B.P. 144—150. 0.075 mm.	19.75 grams $n_D^{25} = 1.4593$, water white	
			Found C=64.17, H=8.95, N=8.64, Cl=trace Calculated for $C_{18}H_{30}N_2O_4$ — C=63.88, H=8.94, N=8.28

Cuts 4 and 5 represent a yield of 66.4% of diisocyanate based on L-lysine ethyl ester dihydrochloride.

5 The other ornithine and lysine diisocyanate alkyl esters of formula A may be prepared in any convenient manner. For example they may be prepared by first reacting the monochloride of ornithine or lysine with the other C₁₋₂₂ carbon atom alkanols in the presence of *p*-toluene sulphonic acid to produce the ornithine or lysine alkyl ester sulphonates, which are then converted to their dihydrochlorides which in turn are reacted with phosgene to produce said diisocyanate alkyl esters. An alternative method of providing the dihydrochloride higher alkyl esters of ornithine or lysine for reaction with phosgene is to first react ornithine with *n*-propanol or lysine with methanol or ethanol in the conventional manner in the presence of HCl to provide the dihydro-

chloride of ornithine *n*-propyl ester or lysine methyl or ethyl ester. These hydrochlorides in turn are tranesterified by heating with a higher alkanol having up to 22 carbon atoms in the presence of HCl as catalyst to produce the dihydrochlorides of the higher alkyl esters of lysine or ornithine. Generally, when the lower alkyl esters are used the phosgenation temperature is between 130° and 160°C whereas when the higher alkyl esters are used the temperature of phosgenation temperature is in the range of 50°C up to 100°C. The reactions may, however, be carried out at lower temperature with an increase in the reaction time.

The following are specific illustrative examples of methods for preparing some of the novel polyureas of this invention and also of some of the polyureas produced thereby. Mesh sizes are U.S. standard.

EXAMPLE 1 Preparation of Lysine Ethyl Ester-Ethylene Diamine Polyurea

		Grams	Moles
Solution I	Ethylenediamine	12.3	0.2
	Dimethylsulphoxide 175 ml.		
Solution II	Lysine diisocyanate ethyl ester	42.2	0.2
	Dimethylsulphoxide 100 ml.		
III	Acetone 600 ml.		

Solution II was added to Solution I keeping the temperature below 50°C with water bath cooling. The resultant solution was then heated to and maintained at 60°C for five hours to assure a high degree of reaction with consequent formation of lysine ethyl ester-ethylene diamine polyurea in high yield. This mass was then poured into III whereby the polymer, which was gummy, precipitated out. The gummy polymer solidified on standing in said III overnight. After filtration and vacuum drying, the yield of polymer was greater than the theoretical value indicating incomplete removal of solvent. After grinding in a mortar and pestle and screening through a 60 mesh screen, the particles of polymer were extracted two times with 400 ml. portions of hot acetone. After filtration and drying, the polymer

weighed 46.5 grams (85.5% yield), and is known as Product 1. Nitrogen Analysis: Calc'd 20.59%; Found, 20.39%.

A 1% solution of Product 1 in dimethyl sulphoxide had a reduced viscosity of 0.33 using a Canon-Fenske Viscosimeter at 25°C. The reduced viscosity was calculated by the formula:

$$\text{Reduced Viscosity} = \frac{t - t_0}{t_0 C}$$

where *t* = time of flow of sample
*t*₀ = time of flow of solvent
C = concentration of polymer in grams per 100 ml. of solution.

EXAMPLE 2

Lysine Methyl Ester -1,3-Propane Diamine Polyurea

		Grams	Moles
Solution I	1,3-Propanediamine	14.8	0.2
	Dimethyl sulphoxide	50	
Solution II	Lysine diisocyanate methyl ester	42.2	0.2
	Dimethyl sulphoxide	142	
III	Acetone 500 ml.		

5 Solution II was added to Solution I with stirring and cooling to keep the temperature below 50°C. After all of Solution II had been added, the mass was heated for sixteen hours at 60°C to complete the reaction. At the end of that time the mass was in the form of a thick solution. The thick solution was poured into III whereupon the polyurea reaction product separated out and lumped. The lumps were broken down after several hours of agitation and filtered. This was resuspended in acetone and washed several times with 400-ml. portions of hot acetone. Yield of lysine methyl ester-1,3-propane diamine polyurea, known as

Product 2, was 47.0 grams (82.5% of theoretical yield).

A 1% solution of Product 2 in dimethyl sulphoxide had a reduced viscosity of 1.32 at 25°C.

Protective Coating.

1 g. of Product 2 dissolved in 19.0 g. of dimethyl sulphoxide was used to coat a glass panel. After driving off the dimethyl sulphoxide by heating at 100°C. in an oven for one hour followed by heating at 140°C. for one hour, a clear, tough, pliable film was left on the glass upon cooling to 25°C.

EXAMPLE 3

Lysine Methyl Ester-1,6-Hexane diamine Polyurea

		Grams
Solution I	Hexamethylene diamine, 70% aq.	16.6
	Water	40.0
Solution II	Lysine diisocyanate methyl ester	21.2
	Methylene dichloride	280.0

30 Solution I was placed in a Waring Blender and Solution II was slowly added with stirring in 10 minutes. Solid polymer formed immediately. A solution of 1:3 water and methanol, 400 ml., was added to the polymer paste. After filtration and washing with the same solvent combination, the product was vacuum dried. The resultant white polymer solid, lysine methyl ester-1,6-hexane diamine

polyurea, known as Product 3, weighed 15.35 grams and analysed 17.10% nitrogen (calculated value 17.05%).

A 1% solution of Product 3 in dimethyl sulphoxide had a reduced viscosity of 0.267 at 25°C.

Product 3, was soluble in formic acid and dimethyl sulphoxide but was only slightly soluble in dimethyl formamide.

EXAMPLE 4
Preparation of Lysine Methyl Ester-1,4-Bis(Aminomethyl)
Cyclohexane Polyurea

		Grams	Moles
Solution I	1,4-Bis-Amino Methyl Cyclohexane	13.6	0.1
	Water 50 ml.		
Solution III	Lysine Diisocyanate Methyl Ester	21.2	0.1
	Methyl Chloride 200 ml.		

5 Solution II was added to Solution I in a Waring Blender in the presence of 50 grams of ice to keep the temperature below 40°C whereupon the polyurea was produced and precipitated out in the form of white solid material. The white solid polymer was washed twice with 400 ml. portions of methanol. After drying, the polyurea, known as Product 4, weighed 30.5 grams (87.5% of theory). The polymer softened at 184°C. and melted at 200°C. on the Kofler Hot Bench. A 1% solution of Product 4 in 88% formic acid had a reduced viscosity of 0.936. 10

EXAMPLE 5
Polyurea from Lysine Diisocyanate Methyl Ester and
m-Phenylene Diamine

		Grams	Moles
Solution I	m-Phenylene Diamine (recrystallized)	5.4	0.05
	Water	20.0	
Solution II	Lysine Diisocyanate Methyl Ester	10.6	0.05
	Methylene dichloride	50.0	

20 In a Waring Blender was placed Solution I. Then Solution II was slowly added, whereupon a tan solid was produced. This was washed twice with acetone after breaking up the solid mass of polymer to smaller pieces. After drying at 70°C. and 0.1 mm. pressure in a vacuum oven for 5 hours, the polyurea, known as Product 5, weighed 16.0 grams (100% of theory). Reduced viscosity (1% of Product 5 in 88% Formic Acid)=0.225 Product 5 softened at 175°C., and melted at 190°C. 25

EXAMPLE 6
Polyurea from Lysine Methyl Ester Free Base and
and Lysine Diisocyanate Methyl Ester [(1-Carbomethoxy Pentamethylene
1.5) Polyurea]

		Grams	Moles
Solution I	Lysine Methyl Ester Dihydrochloride	23.6	0.1
	Water 750 ml.		
Solution II	Lysine Diisocyanate Methyl Ester	21.3	0.1
	Methylene dichloride 1000 ml.		
Solution III	Sodium Hydroxide	8.0	
	Water 250 ml.		

The three solutions were cooled individually to 10°C. Solution II was placed in a 1-gallon Waring Blender. Solutions I and III were added simultaneously to the Blender with stirring in a one-minute period. After stirring for 3 more minutes, the heavy creamy mass was poured into 4 litres of water at 50°C.

The methylene dichloride was evaporated slowly at this temperature. Two more washes with 4-litre portions of hot water kept at

50°C. for a total of three hours served to remove all salts and solvent. The white filtered polyurea produced was dried at 80°C. at 0.1 mm. The dry polyurea, known as Product 6, weighed 40.4 grams (90% of theory). This polyurea softened at 134°C and melted at 150°C.

A 1% solution of Product 6 in dimethyl sulphoxide solvent had a reduced viscosity of 1.31.

EXAMPLE 7

Hydrolysis of Lysine Ethyl Ester-Ethylene Diamine Polyurea (Product 1) to the Free Acid Form of the Polymer

		Grams	Moles
I	Product 1	5.44	0.02
II	Dimethyl Sulphoxide	50.0	
III	Sodium Hydroxide	0.8	0.02
	Water	10.0	

I was dissolved in II in a 250 ml. beaker. Using a Beckmann pH meter, the alkaline solution III was added slowly at 25°C. so that the pH was kept below 10.4. After the last addition of III, the solution was kept for 1 hour at 25°C. with no change in pH whereby the methyl groups were replaced by sodium. The solution of the polyurea sodio-salt, known as Product S—1, was diluted with 100 ml. of water and neutralized with 10% aqueous HCl to pH 3.0. The viscous liquid after washing twice with water still had the odour of dimethyl sulphoxide. The product was redissolved in 20 ml. of 5% aqueous NaOH solution and diluted to 75 ml. with water.

The polymer free acid was precipitated by the addition of 10% aqueous HCl to pH 2.0. After several washings with water, the polyurea free acid was dried at 60—70°C. at 1.0 mm. pressure. The X and R in said product, known as Product 7, were hydrogen and C₂H₅, respectively. Said Product weighed 3.1 grams (51% of theoretical).

Carboxylic acid equivalent weight was 257.0 (Theory is 258.0). A 1% solution of Product 7 in dimethyl sulphoxide had a reduced viscosity of 0.30. The Product 7 softened at 150°C. and melted at 173°C. on the Hot Bench.

EXAMPLE 8

Hydrolysis of Product 3 to its Polymer Free Acid

		Grams	Moles
Suspension I	Product 3	3.3	0.01
	Water	20.0	
	t-Butanael	20.0	
Solution II	NaOH	0.4	0.01
	Water	10.0	

Solution II was added to suspension I in two hours at 60—70°C maintaining the pH below 10.5 throughout whereupon the suspension is converted to a clear solution and

then silky crystals precipitated out. After removal of the solid particles by filtration, the filtrate which was recovered contained polyurea sodio-salt known as Product S—3. It

was acidified with 10% aqueous HCl whereupon the polyurea free acid was formed and precipitated out. After soaking in water for several hours, the polymer hardened and was filtered. The last traces of chloride ion was removed by water washing. The solid polymer was oven dried at 60°C. at 0.1 mm. pressure, and is known as Product 8.

Carboxylic acid equivalent weight was 404.5

(calculated for 100% hydrolysis = 314.4). Thus 78% of the carboxylic ester groups were converted to carboxylic groups in the polymer side chains.

A 1% solution of Product 8 in dimethyl sulfoxide had a reduced viscosity of 0.126.

The Product 8 softened at 140°C. and melted at 153°C. on the Kofler Hot Bench.

EXAMPLE 9

Hydrolysis of Ester Side Chain of Product 4

		Grams	Moles
Solution I	Product 4	8.0	0.025
	Dimethyl sulphoxide		120.0
Solution II	NaOH	1.03	0.025
	Water	10.0	

Solution II was added to solution I in 20 minutes keeping the pH below 10.4. The reaction solution was kept at 25°C. for one hour and then diluted with 100 ml. of water whereby the methyl radicals were replaced by sodium. The sodium salt of the polymer acid, known as Product S—4, was converted to the free acid polymer by the addition of 10% aqueous HCl until the pH was 2.0. A yield of 6.5 grams (85% of theoretical) of the polymer free acid, known as Product 9, was

obtained by first breaking up the polymer to small particles, and washing until the filtrate was chloride-free, followed by drying at 58°C. and 0.1 mm. pressure in a vacuum oven.

Product 8 softened at 220°C. and melted at 232°C.

The carboxylic acid equivalent weight was 455 (theory for 180% by hydrolysis of ester = 306).

The reduced viscosity (1% of Product 9 in 88% HCOOH) was 0.155.

EXAMPLE 10

Hydrolysis of Product 5

		Grams	Moles
I	Product 5	22.4	0.05
Solution II	Sodium Carbonate	11.9	0.11
	Water	125.0	

To Product 5 was added solution II and stirred at 50°C. for 48 hours. All but a small fraction of larger particles of Product 5 went into solution. The solution was filtered and the clear filtrate was recovered and contained the polyurea sodio-salt, known as Product S—5. The filtrate was neutralized to pH 3.0 with 10% aqueous HCl. The white precipitate was washed free of chloride ions with distilled water. After drying at 50°C overnight in a vacuum oven, the polymer free acid, known as

Product 10, weighed 12.0 grams (59% of theoretical).

Carboxylic acid equivalent weight was 382. This indicates 45% of the ester groups were hydrolysed to the acid.

The reduced viscosity of a 1.0% solution of Product 10 in dimethyl sulphoxide was 1.0.

The partially hydrolysed free acid softened at 153°C. and melted at 178°C. on the Kofler Hot Bench.

EXAMPLE 11

Preparation of Ornithine Hexyl Ester-Ethylene Diamine Polyurea, its Sodio Salt and Free Acid

		Grams	Moles
Solution I	Ethylene diamine	12.3	0.2
	Dimethylsulphoxide 175 ml.		
Solution II	Ornithine Diisocyanate hexyl ester	39.4	0.2
	Dimethyl sulphoxide 100 ml.		
III	Acetone 500 ml.		

The procedure of Example 1 is followed but using above recited components, whereby the polyurea, known as Product 11 was obtained. The procedure of Example 7 is then followed, but Product 1 was replaced by 5 grams of Product 11 whereby there was first produced the sodio salt, known as S—6, and then the corresponding polyurea free acid known as Product 12.

Said polyureas of this invention find application in a number of different fields. Some of them find especial use in films as such or as coatings, e.g. for paper, metal foils and glass fabric, and others find especial use as soil suspension agents in laundering or other compositions to be used for that purpose. The polyureas, in which X, in each of the units is a higher alkyl radical are substantially water-insoluble and are useful as binding and coating agents for matte or woven glass fabrics and are also useful as coating agents for other sheet material and in addition are useful per se in film form for packaging. The polyureas in which X is sodium in each of the units are useful as soil suspension agents and also carbon particle suspension agents in aqueous media and find use in laundering to prevent the re-deposition of foreign or soil particles which have been separated from the material being laundered and are in suspension in the course of laundering.

The polyureas, in which X in each of their units is an alkyl radical, and especially those wherein X in each unit is a lower alkyl radical, are useful as binding and non-dusting coating agents for laundry detergent tablets containing an alkaline material, such as caustic soda, as a component thereof and the polyureas wherein X of each of their units is hydrogen are useful for the same purpose. Depending upon the particular X in the recurring units of the individual polyureas, that is whether they be solely alkyl, hydrogen or alkali metal or a combination of 2 or 3 of them, all of said polyureas are useful as coating or binding agents, some of which are of especial value, when they are to serve merely as temporary agents for that purpose and are readily removable therefrom when desired and all of them are useful as binding and coating agents for laundry detergents containing caustic as a component.

The following example illustrates the soil suspension properties of some of the polyureas of this invention.

EXAMPLE B.

Soil Suspension Test.

The sodium salts, Products S—1, S—3, S—4 and S—5 all had soil suspension activity. Product S—1 illustrates this property.

		Grams	Moles
I	Product S—1	0.258	0.001
II	NaOH	0.040	0.001
	Water	10.0	

A solution of (Product S—1), a polymer acid sodium salt was made by adding II to I and shaking. Upon dilution to 56 ml., this contained 0.05 grams of polymer in 10 ml. of solution. A suspension of 3.5 grams of activated

carbon in 200 ml. of water was shaken and 21 ml. portions poured immediately into four 25 ml. graduate cylinders. To each of three of these cylinders was added 0.1, 1.0, and 4.0 ml. of the polymer solution above. After

diluting to 25 ml. with water, they were stoppered, shaken and permitted to stand at 25°C. The carbon in the blank containing no resin

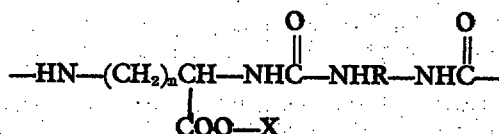
settled to the half-way mark in 80 seconds. The carbon in the other three cylinders settled as shown in the table below:

% Polymer In Solution	ML. of Stock Solution	Carbon Demarcation Line After		
		17 Hours	25 Hours	43 Hours
0.002	0.1	19.0 ml.	17.0 ml.	12.5 ml.
0.02	1.0	23.0 ml.	23.0 ml.	21.0 ml.
0.08	4.0	24.0 ml.	24.0 ml.	23.0 ml.

10 The suspension containing 0.002% polymer salt had settled only 7.0 ml. in 25 hours. After 43 hours the carbon had settled below the 12.5 ml. line. The more concentrated solutions maintained the carbon in suspension even after 43 hours.

15 **WHAT WE CLAIM IS:—**

1. A polyurea consisting essentially of recurring units having the generic formula:



20 in which X is a hydrogen or alkali metal atom or a $\text{—CH}_2\text{—R}_1$ radical where R_1 is a hydrogen atom or a $\text{C}_1\text{—C}_{21}$ alkyl radical; n is 3 or 4; and R is a $\text{C}_2\text{—C}_{10}$ divalent hydrocarbon group, either unsubstituted or carboalkyl-substituted, and the variables can be the same in all the units or differ from unit to unit.

25 2. A polyurea as claimed in claim 1, in which X is $\text{—CH}_2\text{—R}_1$, where R_1 is as defined in claim 1.

30 3. A polyurea as claimed in claim 1, in which X is methyl.

4. A polyurea as claimed in claim 1, in which X is sodium.

5. A polyurea as claimed in claim 1, in which X is hydrogen.

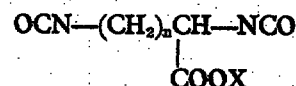
35 6. A polyurea as claimed in claim 1, in which X is some of the recurring units is sodium and in the others is a hydrogen atom or a $\text{—CH}_2\text{—R}_1$ radical, where R_1 is as defined in claim 1.

40 7. A polyurea as claimed in claim 1, in which X in some of the recurring units is methyl and in the others is sodium.

45 8. A polyurea as claimed in claim 1, in which X in some of the recurring units is sodium and in the others is hydrogen.

9. A polyurea as claimed in claim 1, in which X in some of said recurring units is sodium, in some of the recurring units is hydrogen, and in the other is a radical $\text{—CH}_2\text{—R}_1$, where R_1 is as defined in claim 1.

10. A method for producing a polyurea comprising reacting a diisocyanate with the generic formula



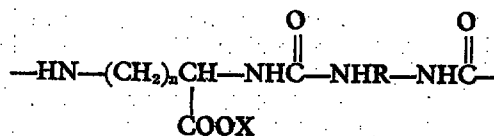
or a mixture of such diisocyanates with a diamine within the generic formula



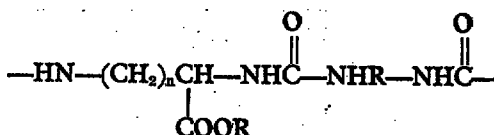
or a mixture of such diamines in which X is an alkyl radical of 1—22 carbon atoms; R is a divalent hydrocarbon group of 2—10 carbon atoms; and n is 3 or 4.

11. A method as claimed in claim 10, in which X is methyl.

12. A method for producing a polyurea consisting essentially of a unit which recurs and is within the generic formula:



where X is as defined in Claim 1 but in at least some of said units is alkali metal, and n is 3 or 4; comprising reacting an alkaline agent whose cation is an alkali metal with a polyurea consisting essentially of a unit which recurs and is within generic formula:



wherein R is an alkyl radical of 1—22 carbon atoms.

13. A method for producing a polyurea consisting essentially of a unit which recurs and is within generic formula:

diluting to 25 ml. with water, they were stoppered, shaken and permitted to stand at 25°C. The carbon in the blank containing no resin

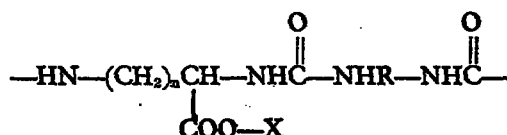
settled to the half-way mark in 80 seconds. 5
The carbon in the other three cylinders settled as shown in the table below:

% Polymer In Solution	Ml. of Stock Solution	Carbon Demarcation Line After		
		17 Hours	25 Hours	43 Hours
0.002	0.1	19.0 ml.	17.0 ml.	12.5 ml.
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15 WHAT WE CLAIM IS:—

1. A polyurea consisting essentially of recurring units having the generic formula:



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25 2. A polyurea as claimed in claim 1, in which X is $\text{—CH}_2\text{—R}_1$, where R_1 is as defined in claim 1.

30 3. A polyurea as claimed in claim 1, in which X is methyl.

4. A polyurea as claimed in claim 1, in which X is sodium.

5. A polyurea as claimed in claim 1, in which X is hydrogen.

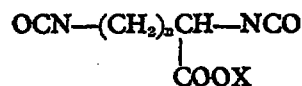
35 6. A polyurea as claimed in claim 1, in which X is some of the recurring units is sodium and in the others is a hydrogen atom or a $\text{—CH}_2\text{—R}_1$ radical, where R_1 is as defined in claim 1.

40 7. A polyurea as claimed in claim 1, in which X in some of the recurring units is methyl and in the others is sodium.

8. A polyurea as claimed in claim 1, in which X in some of the recurring units is sodium and in the others is hydrogen.

45 9. A polyurea as claimed in claim 1, in which X in some of said recurring units is sodium, in some of the recurring units is hydrogen, and in the other is a radical $\text{—CH}_2\text{—R}_1$, 50 where R_1 is as defined in claim 1.

10. A method for producing a polyurea comprising reacting a diisocyanate with the generic formula



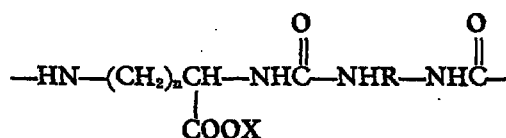
or a mixture of such diisocyanates with a diamine within the generic formula



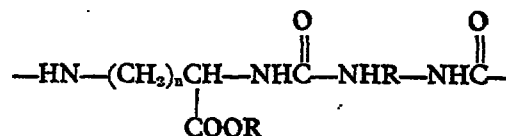
or a mixture of such diamines in which X is an alkyl radical of 1—22 carbon atoms; R is a divalent hydrocarbon group of 2—10 carbon atoms; and n is 3 or 4.

11. A method as claimed in claim 10, in which X is methyl.

12. A method for producing a polyurea consisting essentially of a unit which recurs and is within the generic formula: 65



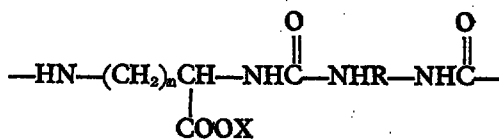
where X is as defined in Claim 1 but in at least some of said units is alkali metal, and n is 3 or 4; comprising reacting an alkaline agent whose cation is an alkali metal with a polyurea consisting essentially of a unit which recurs and is within generic formula: 70



wherein R is an alkyl radical of 1—22 carbon atoms. 75

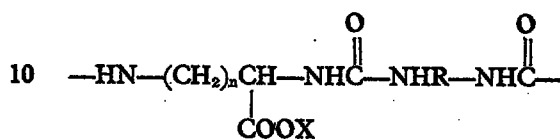
13. A method for producing a polyurea consisting essentially of a unit which recurs and is within generic formula:





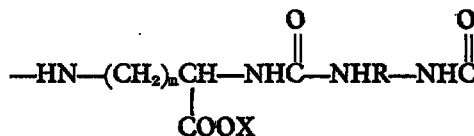
where X is as defined in Claim 1 but in at least some of said units is hydrogen and n is 3 or 4; comprising hydrolysing a C_{1-22} alkyl ester thereof under acidic conditions.

- 5 14. The method that comprises at least partially hydrolysing with sodium hydroxide a polyurea consisting essentially of a recurring unit of generic formula:



in which X is a C_{1-22} alkyl radical and n is

3 or 4 to produce a polyurea consisting essentially of a recurring unit of formula:



in which X in some of said units is sodium 15 and in the others is an alkyl radical of 1—22 carbon atoms and n is 3 or 4.

15. A method for producing a polyurea as claimed in Claim 1, substantially as hereinbefore described in any one of the foregoing 20 Examples.

16. A polyurea when prepared by a process as claimed in any one of Claims 10—15.

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