

PATENT SPECIFICATION

NO DRAWINGS

1.180.835



Date of Application (No. 12771/67) and filing Complete Specification: 17 March, 1967.

Application made in Japan (No. 16845) on 17 March, 1966.

Complete Specification Published: 11 Feb., 1970.

Index at acceptance:—C3 R(32B1, 32B2, 32C6X, 32C10, 32C12, 32C13P, 32C23, 32D1, 32D2, 32D5, 32D6A, 32D6C, 32D6D, 32D6E, 32E1, 32G1, 32H1, 32H5F, 32H8, 32J2Y, 32L4C, 32L5X, 32L6G); C3 C1E2

International Classification:—C 08 g 22/48

COMPLETE SPECIFICATION

Intumescent Polyurethane Coating Compositions

We, TAKEDA CHEMICAL INDUSTRIES, LTD., a Company organised under the Laws of Japan, of 54, 4-chome, Jusonishino-cho, Higashiyodogawa-ku, Osaka, Japan, 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:—

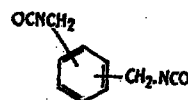
This invention relates to two-component intumescent polyurethane coating compositions.

Previously proposed — two component coating compositions contain, as the first component, a tolylene diisocyanate or a diphenylmethane diisocyanate as the isocyanate component and, as the second component, a suitable combination of polyol composition, catalyst, blowing agent and the like, and these components are sometimes used by spraying the first and second components simultaneously. However, these polyurethane coating compositions, suffer from fatal defects from an industrial point of view in that their so-called pot-life is extremely short — from 30 seconds to 3 minutes — because a foaming reaction takes place soon after admixture of the two components, and in that the coating film produced therefrom is discoloured soon after its exposure to atmosphere.

We have found that the use of a polyurethane prepolymer containing 10 to 35 percent by weight of NCO radicals, which is derived from an ω, ω' -diisocyanate dimethyl benzene and a polyol, in a combination with polyether polyol or polyester polyol can lead to an intumescent polyurethane coating composition having a longer pot-life and being capable of producing a foamed coating film which is not discoloured even after exposure to atmosphere for a long period of time.

According to the invention there is provided an intumescent polyurethane coating composition,

which comprises (1) as the first component, a polyurethane prepolymer having from 10 to 35 weight percent of NCO radicals, which is derived by a reaction of ω, ω' -diisocyanate dimethyl benzene of the formula



and a polyol, and (2) as the second component, a mixture of polyether or polyester polyol in an amount such as to provide an NCO:OH ratio of approximately 1, a polymerisation catalyst, a blowing agent and a foam regulating agent.

The ω, ω' - diisocyanate dimethyl benzenes represented by the above formula include ω, ω' - diisocyanate - 1,2 - dimethyl benzene, ω, ω' - diisocyanate - 1,3 - dimethyl benzene and ω, ω' - diisocyanate - 1,4 - dimethyl benzene. In the present invention, any of these isomers or any mixture thereof may be used, but a mixture of 1,3-isomer and 1,4-isomer, especially a mixture of 60 to 90 weight percent of 1,3-isomer and 10 to 40 weight percent of 1,4-isomer is preferred.

The polyol to be used to prepare the first component is preferably a relatively high molecular weight polyether polyol or polyester polyol.

The polyether polyol employed in this invention, can be obtained by addition polymerisation of one or more alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide or styrene oxide, to one or more polyols, as initiator, such as ethylene glycol, diethylene glycol, propylene glycol, glycerol, trimethylol propane, hexane triol, pentaerythritol, sorbitol, sucrose, mannitol, mannitan, or sorbitan, or to amines such as ethylene diamine, propylene

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diamine, ethanolamine, under alkaline or acid conditions.

These polyether polyols may be prepared in a known manner as described in "High Polymer Vol. XIII. Polyethers Part 1" (1963) by Norman G. Gaylord, published by Interscience Publishers, New York, N.Y.

As polyester polyol in this invention, there may be employed a product obtained by the reaction of one or more polyols such as ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, butylene glycol, trimethylol propane, glycerol, hexane triol or pentaerythritol with one or more polycarboxylic acids such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, or their acid anhydrides.

These polyester polyols are prepared in a known manner as described in "Polyesters and Their Application", April 1959, published by Bjorksten Research Lab. Inc., New York, New York.

Modified polyether polyols or polyester polyols (e.g. modified by castor oil may also be used. For obtaining a flame proofing coating film, conventional polyether polyols or polyester polyols containing halogen or a phosphorus atom may be used in place of or together with the above-mentioned polyols.

These polyether polyols or polyester polyols to be reacted with the ω, ω' -diisocyanate dimethyl benzene are preferably those having a OH number of 200 to 550.

In place of the relatively high molecular weight polyols, low molecular weight polyols having molecular weights not exceeding 150, such as trimethylol propane, 1,2,6-hexane triol, ethyleneglycol, butylene glycol, 2,2,4-trimethyl pentanediol, may be used.

The prepolymer of the first component of the present invention is prepared by reacting one or more of above-mentioned polyols and one or more of the ω, ω' -diisocyanate dimethyl benzenes in such a ratio that the NCO content of the prepolymer to be produced is from 10 to 35 weight percent, at a room temperature or at an elevated temperature, preferably, in an inert gas stream. Additionally the above state ratio of the polyol to ω, ω' -diisocyanate dimethyl benzene can be determined by considering the OH number of the polyol to be used.

The second component of the present composition chiefly comprises a polyester polyol or polyether polyol. The polyester polyol or polyether polyol is preferably selected from those defined above. The second component also contains a blowing agent, a foam regulating agent and a catalyst other than the polyether polyol or polyester polyol.

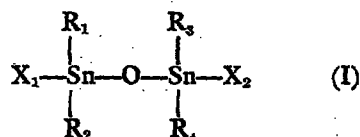
Any of the conventional blowing agents

may be used, for example, water or halogenated hydrocarbons.

Particularly useful blowing agents are the halogenated hydrocarbons which have comparatively high boiling points such as trichloromonofluoromethane and tetrachlorodifluoro ethane. When inert compounds such as halogenated hydrocarbons are used as blowing agents, they may be incorporated in the first component.

Any of the foam regulating agents which have been conventionally used for the purpose of regulating rigid foams may be conveniently employed in the present invention, for example, silicone oil or nonionic surfactants.

As the catalysts, any of those which have heretofore been used in the production of rigid foams, for example, tertiary amines or organic tin compounds, may be successfully used. Tetraalkyldistannoxane, which has the following general formula, is one of the most desirable catalysts,



wherein X_1 is a halogen atom, a hydroxyl radical, an alkoxy radical having from 1 to 3 carbon atoms, a formyloxy radical, an alkylcarbonyloxy radical, a cyanoacetoxy radical, an $-NCO$ radical or an NCS radical, X_2 is a hydroxyl radical, an alkoxy radical having from 1 to 3 carbon atoms, a formyloxy radical, an alkylcarbonyloxy radical, a cyanoacetoxy radical, an NCO radical or an NCS radical, and each of R_1, R_2, R_3 and R_4 is an alkyl radical having from 1 to 4 carbon atoms.

Typical examples of the tetraalkyl distannoxanes are as follows:

- (1) Tetrabutyl - 1 - chloro - 3 - hydroxy - distannoxane, 100
- (2) Tetrabutyl - 1,3 - diacetoxy - distannoxane,
- (3) Tetrabutyl - 1,3 - distearoyloxy - distannoxane, 105
- (4) Tetrabutyl - 1,3 - diformyloxy - distannoxane,
- (5) Tetrabutyl - 1,3 - di - (2 - ethylhexanoyloxy) - distannoxane, 110
- (6) Tetrapropyl - 1 - chloro - 3 - hydroxy - distannoxane,
- (7) Tetrabutyl - 1,3 - dilauroyloxy - distannoxane,
- (8) Tetraethyl - 1 - chloro - 3 - hydroxy - distannoxane, 115
- (9) Tetramethyl - 1 - chloro - 3 - hydroxy - distannoxane,
- (10) Tetrapropyl - 1,3 - diacetoxy - distannoxane, 120
- (11) Tetrabutyl - 1,3 - diacryloxy - distannoxane,

- | | | | |
|----|--|---|-----|
| | (12) Tetrabutyl - 1,3 - dicyanoacetoxy - distannoxane, | (44) Tetrabutyl - 1 - monoethylmaleoyloxy - 3 - distannoxane, | 65 |
| | (13) Tetrabutyl - 1,3 - dibenzyloxy - distannoxane, | (45) Tetrabutyl - 1 - stearoyloxy - 3 - ethoxy - distannoxane, | |
| 5 | (14) Tetraethyl - 1,3 - diacetoxy - distannoxane, | (46) Tetrabutyl - 1 - formyloxy - 3 - ethoxy - distannoxane, | 70 |
| | (15) Tetramethyl - 1,3 - distearoyloxy - distannoxane, | (47) Tetrapropyl - 1 - acetoxy - 3 - methoxy - distannoxane, | |
| 10 | (16) Tetramethyl - 1,3 - diacetoxy - distannoxane, | (48) Tetrabutyl - 1 - acetoxy - 3 - propoxy - distannoxane, | |
| | (17) Tetrabutyl - 1 - acetoxy - 3 - hydroxy - distannoxane, | (49) Tetrapropyl - 1 - lauroyloxy - 3 - methoxy - distannoxane, | 75 |
| | (18) Tetrabutyl - 1 - formyloxy - 3 - hydroxy - distannoxane, | | |
| 15 | (19) Tetrapropyl - 1 - acetoxy - 3 - hydroxy - distannoxane, | | 80 |
| | (20) Tetrabutyl - 1,3 - bis - (monomethylmaleoyloxy) - distannoxane, | | |
| | (21) Tetrabutyl - 1 - lauroyloxy - 3 - hydroxy - distannoxane, | | |
| 20 | (22) Tetraethyl - 1 - acetoxy - 3 - hydroxy - distannoxane, | | 85 |
| | (23) Tetraethyl - 1 - (2 - ethylhexanoyloxy) - 3 - hydroxy - distannoxane, | | |
| 25 | (24) Tetrabutyl - 1 - chloro - 3 - methoxy - distannoxane, | | 90 |
| | (25) Tetrabutyl - 1 - chloro - 3 - ethoxy - distannoxane, | | |
| 30 | (26) Tetrabutyl - 1 - chloro - 3 - propoxy - distannoxane, | | |
| | (27) Tetrapropyl - 1 - chloro - 3 - methoxy - distannoxane, | | 95 |
| | (28) Tetraethyl - 1 - chloro - 3 - methoxy - distannoxane, | | |
| 35 | (29) Tetrabutyl - 1,3 - diisocyanate - distannoxane, | | |
| | (30) Tetrabutyl - 1,3 - diisocyanate - distannoxane, | | 100 |
| 40 | (31) Tetrapropyl - 1,3 - diisocyanate - distannoxane, | | |
| | (32) Tetraethyl - 1,3 - diisocyanate - distannoxane, | | 105 |
| | (33) Tetramethyl - 1,3 - diisocyanate - distannoxane, | | |
| 45 | (34) Tetrapropyl - 1,3 - diformyloxy - distannoxane, | | |
| | (35) Tetraethyl - 1,3 - diformyloxy - distannoxane, | | 110 |
| 50 | (36) Tetramethyl - 1,3 - diformyloxy - distannoxane, | | |
| | (37) Tetramethyl - 1 - acetoxy - 3 - hydroxy - distannoxane, | | 115 |
| | (38) Tetraethyl - 1 - formyloxy - 3 - hydroxy - distannoxane, | | |
| 55 | (39) Tetrapropyl - 1 - formyloxy - 3 - hydroxy - distannoxane, | | |
| | (40) Tetrabutyl - 1 - acetoxy - 3 - methoxy - distannoxane, | | 120 |
| | (41) Tetrabutyl - 1 - formyloxy - 3 - methoxy - distannoxane, | | |
| 60 | (42) Tetrabutyl - 1 - acetoxy - 3 - ethoxy - distannoxane, | | |
| | (43) Tetrabutyl - 1,3 - dioleyloxy - distannoxane, | | 125 |

In the present composition, a ratio of the first component to the second one is selected so as to make the total OH radicals in the second component nearly equal to the total NCO radicals in the first component. Namely, the molar ratio of NCO/OH in the whole composition may preferably be 0.95 to 1.10.

The amount of the polymerisation catalysts to be incorporated may be from 0.005 to 0.4 weight percent of the whole composition. The amount of the blowing agent and foam regulating agent may be selected within a conventional range.

Additives may also be incorporated in the present composition such as pigments, dyes, solvents, viscosity regulators, fillers, heat resistance promoter, fire proofing agents, antioxidants, thixotropic agents, cross-linking agents, water-proofing agents and germicides. While these additives are generally incorporated in the second component mentioned above, it is possible, in certain cases to add them to the first component.

The intumescent polyurethane coating composition is manufactured by admixing the first component and the second one in a proper ratio as mentioned above.

Thus manufactured composition has rather long pot life, and therefore it is very easily handled over a long period of time.

The composition may be applied by any of conventional means such as brushing, flow-coating, spraying, etc.

The composition so applied can be cured completely even at room temperature or preferably by heating, to give foamy polyurethane coating film which does not discolour after exposure to atmosphere for a long period of time. The cured composition has high impact-resistance, high heat resistance and good brittleness.

For the purpose of a better understanding of this invention, the following examples are given. However, it is to be understood that the invention is not limited to these examples.

In these examples, the amount are expressed in parts by weight unless otherwise stated. Parts by weight bear the same relation to parts by volume as do gram to millilitres.

EXAMPLE 1

(A) Synthesis of prepolymer

- 1) To 1936 parts of a mixture of 75 weight percent of ω,ω' - diisocyanate - 1,3 - dimethyl benzene and 25 weight percent of ω,ω' - diisocyanate - 1,4 - dimethyl benzene were added, in a stream of nitrogen and with stirring, 400 parts of sucrose-propylene oxide polyether (OH number — 465), and the reaction allowed to proceed at 90°C for 40 minutes. The resulting polyurethane prepolymer had 31 weight percent of NCO radicals and a viscosity of 135 cps (20°C).
- 2) To 1256 parts of a mixture of 78 weight percent of ω,ω' - diisocyanate - 1,3 - dimethyl benzene and 22 weight percent of ω,ω' - diisocyanate - 1,4 - dimethyl benzene were added 400 parts of phosphorus-containing diol (Vircol—82, Virginia Carolina Chem, Corp. in U.S.A. OH number 215), and the reaction conducted in a stream of nitrogen with stirring at 90°C for 90 minutes. The resulting polyurethane prepolymer had 31 weight percent of NCO radicals and a viscosity of 35 cps (20°C).

3) Control

To 1468 parts of a mixture of 80 weight percent of 2,4-tolylene diisocyanate and 20 weight percent of 2,6-tolylene diisocyanate were added, in a stream of nitrogen with constant stirring, 400 parts of sucrose-propylene oxide polyether (OH number — 465), and the reaction allowed to proceed at 90°C for 40 minutes. The resulting polyurethane prepolymer had 31 weight percent of NCO radicals and a viscosity of 3500 cps (20°C).

(B) Production of polyurethane foam coating composition.

The first and second components given in Table 1 were admixed together, and the mixture applied by brushing. The time during which the mixture may be handled (i.e. pot life) and the properties of the resulting film were evaluated.

The results are shown in Table 1.

In the table, codes I, II and III in the prepolymer columns represents the products prepared in (1), (2) and (3) under "Synthesis of Prepolymer".

TABLE 1
Formulations and Properties of resulting intumescent polyurethane coating compositions.

Formulation	First Component	Type	The present invention								Control	
			1	2	3	4	5	6	7	8		
		Amount (parts)	I	II	I	I	II	I	III	III		
			116	120	116	116	120	116	123	123		
		Sucrose-propylene oxide polyether (OH-456)	100	100	100	100	100	100	100	100		
		Tris-beta-chloroethyl phosphate		20			20					
		Trichloromonofluoromethane	30	30								
		Trichlorotrifluoroethane			30	30	30	30	30	30		
		Silicone foam regulator	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		
		Triethylene diamine	1.0		0.33				0.07			
		Tetrabutyl diacetoxystannoxane		0.04		0.02	0.02	0.02				
		Silica powder						8				

TABLE 1 (Continued)

	The present invention								Control	
	1	2	3	4	5	6	7	8		
Pot life (min.) at room temp. (25°C.)	15	90	60	135	240	120	240	7		
Curing time at room temp. (min.)	80	200	180	240	300	220	24	80		
Curing time by warming at 60°C (min.)	24	18	17	19	24	20	9	7		
Weather resistance with Weatherometer (5 days)	not coloured								Coloured yellow	
Outdoor exposure (60 days)	Not coloured								Coloured Yellow	
Heat resistance (110°C)	Good								—	
Brittleness	Good								Very poor	
Impact resistance	Good								Not good	

Reactivity

Properties of film

EXAMPLE 2

(A) Synthesis of prepolymer

To 590 parts of a mixture of 78 weight percent of ω,ω' -diisocyanate - 1,3 - dimethyl benzene and 22 weight percent of ω,ω' -diisocyanate - 1,4 - dimethyl benzene were added, in a nitrogen stream and with constant stirring, 134 parts of trimethylol propane and

45.5 parts of 1,3-butylene glycol, and the reaction conducted at 80°C for 1 hour. The resulting polyurethane prepolymer had 12 weight percent of NCO radicals.

(B) The first and second components of Table 2 were mixed together, and the pot-life and the properties of the resulting film evaluated.

The results are summarised in Table 2.

TABLE 2

Formulation	First Component	Prepolymer	335 parts
		Trichloromonofluoro methane	40 parts
	Second Component	Sucrose-propylene oxide polyether (OH number . . . 530)	100 parts
		Tris-beta-chloroethyl phosphate	20 parts
		Silicone foam regulator	22 parts
		Tetrabutyl-1-chloro-3-hydroxy distannoxane	0.025 part
Reactivity	Pot-life at room temp. (25°C.)		160 min.
	Curing time (25°C)		260 min.
	Curing time by warming at 60°C.		20 min.
Properties of film	Weather resistance (60 days)		not coloured
	Impact resistance		good
	Heat resistance (110°C.)		good

WHAT WE CLAIM IS:—

1. An intumescent polyurethane coating composition, which comprises (1) as the first component, a polyurethane prepolymer having from 10 to 35 weight percent of NCO radicals, which is derived by a reaction of ω, ω' -diisocyanate dimethyl benzene of the formula



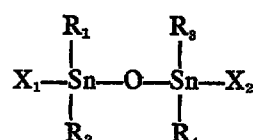
and a polyol, and (2) as the second component, a mixture of polyether polyol or polyester polyol in an amount such as to provide an NCO:OH ratio of approximately 1, a polymerisation catalyst, a blowing agent and a foam regulating agent.

2. A composition as claimed in Claim 1, wherein the polyol of the first component is a polyether polyol or polyester polyol, having an OH number of from 200 to 550, and the polyether polyol or polyester polyol in the second component has an OH number of from 200 to 550.

3. A composition as claimed in Claim 1, wherein the polyol of the first component is a polyol having a molecular weight not exceeding 150.

4. A composition as claimed in any preceding claim, wherein the ω, ω' -diisocyanate dimethyl benzene is a mixture of 60 to 90 weight percent of ω, ω' -diisocyanate - 1,3 - dimethyl benzene and 10 to 40 weight percent of ω, ω' -diisocyanate - 1,4 - dimethyl benzene.

5. A composition as claimed in any preceding claim, wherein the catalyst in the second component is a tetraalkyl distannoxane of a formula



wherein X_1 is a halogen atom, a hydroxyl radical, an alkoxy radical having from 1 to 3 carbon atoms, a formyloxy radical, an alkyl-carbonyloxy radical, a cyanoacetoxy radical, an NCO radical or an NCS radical, X_2 is a hydroxyl radical, an alkoxy radical having from 1 to 3 carbon atoms, a formyloxy radical, an alkylcarbonyloxy radical, a cyanoacetoxy radical, an NCO radical or an NCS radical, and each of R_1 , R_2 , R_3 and R_4 is an alkyl radical having from 1 to 4 carbon atoms.

6. A composition as claimed in any preceding claim, wherein the first component also includes an inert blowing agent.

7. An intumescent polyurethane coating

TABLE 2

Formulation	First Component	Prepolymer	335 parts
		Trichloromonofluoro methane	40 parts
	Second Component	Sucrose-propylene oxide polyether (OH number . . . 530)	100 parts
		Tris-beta-chloroethyl phosphate	20 parts
		Silicone foam regulator	22 parts
		Tetrabutyl-1-chloro-3-hydroxy distannoxane	0.025 part
Reactivity	Pot-life at room temp. (25°C.)		160 min.
	Curing time (25°C)		260 min.
	Curing time by warming at 60°C.		20 min.
Properties of film	Weather resistance (60 days)		not coloured
	Impact resistance		good
	Heat resistance (110°C.)		good

WHAT WE CLAIM IS:—

1. An intumescent polyurethane coating composition, which comprises (1) as the first component, a polyurethane prepolymer having from 10 to 35 weight percent of NCO radicals, which is derived by a reaction of ω, ω' -diisocyanate dimethyl benzene of the formula



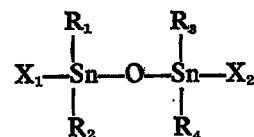
- and a polyol, and (2) as the second component, a mixture of polyether polyol or polyester polyol in an amount such as to provide an NCO:OH ratio of approximately 1, a polymerisation catalyst, a blowing agent and a foam regulating agent.

2. A composition as claimed in Claim 1, wherein the polyol of the first component is a polyether polyol or polyester polyol, having an OH number of from 200 to 550, and the polyether polyol or polyester polyol in the second component has an OH number of from 200 to 550.

3. A composition as claimed in Claim 1, wherein the polyol of the first component is a polyol having a molecular weight not exceeding 150.

4. A composition as claimed in any preceding claim, wherein the ω, ω' -diisocyanate dimethyl benzene is a mixture of 60 to 90 weight percent of ω, ω' -diisocyanate - 1,3 - dimethyl benzene and 10 to 40 weight percent of ω, ω' - diisocyanate - 1,4 - dimethyl benzene.

5. A composition as claimed in any preceding claim, wherein the catalyst in the second component is a tetraalkyl distannoxane of a formula



- wherein X_1 is a halogen atom, a hydroxyl radical, an alkoxy radical having from 1 to 3 carbon atoms, a formyloxy radical, an alkylcarbonyloxy radical, a cyanoacetoxy radical, an NCO radical or an NCS radical, X_2 is a hydroxyl radical, an alkoxy radical having from 1 to 3 carbon atoms, a formyloxy radical, an alkylcarbonyloxy radical, a cyanoacetoxy radical, an NCO radical or an NCS radical, and each of R_1, R_2, R_3 and R_4 is an alkyl radical having from 1 to 4 carbon atoms.

6. A composition as claimed in any preceding claim, wherein the first component also includes an inert blowing agent.

7. An intumescent polyurethane coating



composition in accordance with claim 1 substantially as described herein with reference to any one of the Examples.

- 5 8. Foamed polyurethane coating film which is prepared by curing the composition as claimed in any preceding claim.

TREGEAR, THIEMANN & BLEACH,
Chartered Patent Agents,
Melbourne House,
Aldwych,
London, W.C.2.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
copies may be obtained.

