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(21) International Application Number: PCT/GB90/00001 (22) International Filing Date: 2 January 1990 (02.01.90) (30) Priority data: 8900028.5 3 January 1989 (03.01.89) GB (71) Applicant (for all designated States except US): MORTON INTERNATIONAL LIMITED [GB/GB]; Lyndean House, Farm Yard, Windsor, Berkshire SL4 1QL (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : LEE, Timothy, Charles, Philip [GB/GB]; 18 Ferndale Drive, Kenilworth, Warwickshire CV8 2PP (GB). LOWE, George, Bernard [GB/GB]; 89 Cropston Road, Anstey, Leicester LE7 7BQ (GB). ROBINSON, Raymond [GB/GB]; 15 Yule Road, Wyken, Coventry (GB).		(74) Agents: BANKES, Stephen, Charles, Digby et al.; Baron and Warren, 18 South End, Kensington, London W8 (GB). (81) Designated States: AU, CA, JP, KR, NO, US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CURING OF POLYSULPHIDES (57) Abstract A method of manufacturing a polysulphide polymer, in particular for use as a sealant in the construction industry and the like. A liquid polysulphide prepolymer is partially cured with an oxidizing curing agent such as calcium peroxide, by adding a controlled amount of water. As the cure reaches the end of its induction stage, before the viscosity rises substantially, the reaction is stopped by dehydrating with a desiccant. This gives a stable liquid prepolymer which can later be cured without an induction period by exposure to moisture and optionally a further curative.		

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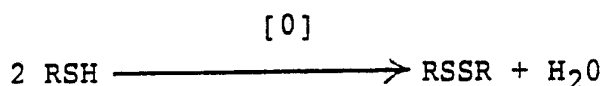
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CURING OF POLYSULPHIDES

This invention relates to the manufacture of polysulphide compositions of the type used, for example, as sealants in glazing and in other applications in the construction industry.

In preparing polysulphide sealants, a mercaptan-terminated polymer, generally a liquid polysulphide of relatively low molecular weight, is reacted with a curing agent, preferably an oxidising agent such as calcium peroxide, to cure it to a solid state. The preferred liquid polysulphide polymers are those having a molecular weight of 1000 - 8000, a viscosity of 10 to 2000 poise and a degree of crosslinking of 2.0 or less. The preferred polymers are those prepared by Morton Thiokol Inc. and known as LP-2, LP-32 etc. The chemistry embodied in this reaction applies to all mercaptan terminated liquid polymers.



Curing agents such as calcium peroxide require the presence of water to activate them. It is therefore possible, instead of using a cumbersome two-part sealant composition, to use a one-part composition of liquid polysulphide and curing agent which is kept free of water until used. Once the sealant is in place it forms a skin and slowly cures to a rubber state through the presence of atmospheric moisture.

One known polysulphide composition comprises 100 parts by weight of liquid polysulphide LP32C (Morton International Inc)

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and 10 parts by weight of calcium peroxide. Such a composition generally takes several days to cure, having a skin time of 72 hours or more. To cure such a composition in a shorter time requires a temperature of 25°C or more and a relative humidity of 95%.

There is therefore a need for polysulphide sealant compositions which can be easily prepared, are stable during storage and which cure in a short time once in position.

The inventors have found that when polysulphides are cured with a curing agent, for example with a strong oxidising agent such as a metal peroxide, the cure generally proceeds in three distinct stages.

The stages are:-

(I) Induction - when little increase in viscosity is noted.

(II) Chain extension and cross linking -- when the viscosity rises rapidly and the system approaches the gel state.

(III) Final cure. The viscosity is beyond the measuring limits of the viscometer. The final stages of polymer network formation take place.

The precise shape of the viscosity-time curve is dependent on many factors such as catalyst type, catalyst level, temperature etc.

The time required for the induction step (I) can vary considerably but in many cases, for example single part sealants based on polysulphide polymers and cured with calcium peroxide, this first step is very long. This is advantageous with respect to storage stability, but a

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disadvantage after application with respect to rate of cure. The reaction between polysulphide polymers and metal peroxides are catalysed by water and as such can be retarded to substantially a zero rate by dehydration.

The present invention consists in a method of making a polysulphide composition wherein a prepolymer having free mercaptan groups is mixed with a curing agent of a type activated by water, characterized in that the composition is subjected to a partial cure with water, the reaction then being stopped by dehydration.

The invention thus provides a technique which allows the reaction to proceed along the path of step I, induction, to a point just prior to commencement of Step II and no further.

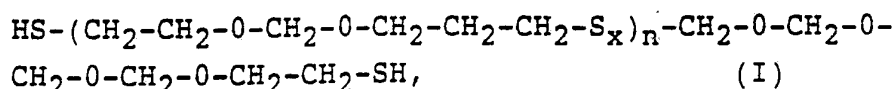
At the completion of Step I the reaction is stopped by rapid dehydration, preferably by the use of molecular sieve. The subsequent exposure of this system to moist air reinitiates the reaction at the commencement of Step II, i.e. there is no longer an induction period.

Suitable molecular sieve types include types 3A, 4A, 13X and 14X.

The stabilised polysulphide polymer, which has reached the end of the induction step is hereafter referred to as "Prereacted" LP polysulphide polymer.

It is possible by the means described above to make stable prereacted LP polymers using ingredients commonly found in single part polysulphide sealants. These polymers blended with other ingredients form sealants which cure more rapidly than conventional polysulphide sealants.

The liquid polysulphides preferred for the purposes of the invention have the general formula:



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wherein x is from 2 to 5 and n is from 10 to 45.

The preferred curing agent is calcium peroxide, but other inorganic or organic oxidizing agents may be used, for example:

- Urea hydrogen peroxide;
- Sodium perborate monohydrate;
- Sodium perborate tetrahydrate;
- Sodium peroxide;
- Manganese dioxide.

Preferred embodiments of the invention will now be described with reference to the accompanying drawings wherein:

Figure 1 shows by means of a viscosity- time curve the course of curing of a typical polysulphide:

Figure 2 shows the induction and cross linking stages and how they are influenced by catalyst levels:

Figure 3 illustrates how viscosity increases with time for six sealant/curing agent systems with different water contingents;

Figure 4 shows directly how the induction time varies with water content;

Figure 5 shows how the induction time varies with the degree of cross-linking;

Figure 6 shows how the induction time varies with the chain length of the polysulphide;

Figure 7 shows how the induction time varies with water content;

Figure 8 shows curing rates for systems at two different temperatures and

Figure 9 is a worklife curve for a prereacted LP system.

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Referring first to Fig. 1, viscosity is plotted against time for a calcium peroxide-cured liquid polysulphide sealant such as LP32c. It can be seen from this that during stage I the viscosity does not rise significantly. The viscosity then rises rapidly in stage II and levels off as the system approaches stage III, the final cure. The viscosity eventually becomes so great that it cannot be measured and the sealant solidifies.

The principle underlying the invention is to add a controlled amount of water to allow the system to cure as far as the dotted line, which corresponds to the end of the induction period T_i . This period is typically about 2 hours but can vary considerably. At the end of the induction period the cure is stopped by means of a desiccant to give a partially liquid polysulphide which is stable provided it is kept dry.

It has been unexpectedly found that such a pre-reacted system when re-exposed to moist air and optionally a further curing agent, cures more quickly than a system of similar formulation using conventional polymers. Thus the prereaction not only gives a fast initiation of cure but appears to render the system self-catalyzing.

The partial cure can be stopped at the end of the induction period by the addition of a desiccant such as a molecular sieve desiccant. The precise length of the induction period can be adjusted by varying the amount of curing agent used and by the use of the desiccant. It has been found that instead of the 10 parts of calcium peroxide per 100 parts of polysulphide conventionally used, 20 to 40% of this amount can be used to give a stable partially cured product which can then be cured rapidly on exposure to atmospheric moisture.

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Preferred embodiments of the invention will be described in more detail in the following examples.

In most of the examples the liquid polysulphide used is LP32c, mentioned above. This has the general formula (I) above, with the following particular parameters:

x (average)	=	2.25
n (average)	=	22
% branching	=	0.5
Viscosity	=	470 poise
Molecular weight		
(Mn)	=	4000.

EXAMPLE 1

A test composition was made up using polysulphide LP32c one hundred wt. parts, calcium peroxide 10 wt. parts, water 2 wt. parts. This was found to have an induction period of 2 hours, a skin time of 2 hours 50 m,minutes and a full cure of about 24 hours. (In the absence of water the induction period is approximately seven days and full cure takes several weeks).

The above formulation was allowed to react for one hour 50 minutes, and the reaction was then stopped by the addition of 10 wt. parts of molecular sieve desiccant. The formulation so prepared was stored in an air tight container, with no air space. Upon reexposure to air, the skinning time of the partially reacted formulation was 10 minutes only.

EXAMPLE 2

For the purpose of preparing the prereacted polysulphide it was considered that 10 parts of calcium peroxide

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might be excessive. Therefore, a series of experiments at different levels of CaO_2 were carried out in which stability and subsequent reactivity were examined.

<u>Test No:</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>
LP32c	100	100	100	100	100
Calcium peroxide	8	6	4	2	0

The level of stability was found to be related to the level of calcium peroxide (not unexpected) but the lowest level of calcium peroxide found to give catalytic cure was 4%. This was shown to be effective not only with further additions of calcium peroxide, but also with other oxidisers such as sodium perborate and urea hydrogen peroxide.

EXAMPLE 3

A liquid polysulphide composition was made up as follows:

Polysulphide LP32c	-	100 wt. parts
MnO_2 curing agent	-	10 wt. parts
Plasticizer HB 40	-	10 wt. parts
Tetramethyl thiuram disulphide (TMTD)	-	0 - 0.5 wt. parts

The viscosity was monitored and plotted against time for four examples with different TMTD contents, the results being shown in Fig. 2. It can be seen from this graph that in the absence of TMTD the system has an induction time of 40-50 minutes, and the addition of 0.1 wt.% TMTD, based on the polysulphide, makes little difference to this. The addition of 0.25 wt.% of TMTD reduces the induction time to

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about 20 minutes and the addition of 0.5 wt.% reduces it still further to about 15 minutes.

EXAMPLE 4

In an LP32c/calcium peroxide system, water was added in amounts of 3 to 6 wt.% based on the polysulphide, to initiate the induction stage of the cure. Viscosity was plotted against time for six samples, and the results are shown in Figure 3. By adding 6 wt.% of water the length of the induction stage can be reduced to 10 minutes. The relationship between water content and induction time is shown more directly in Figure 4.

EXAMPLE 5

Compositions similar to those of Example 4 were made up using the following different liquid polysulphides, to establish the relationship between the degree of cross-linking of the polymer and the induction time:

Liquid polysulphide	% cross linking.
LP 541	0.0
LP 32c	0.5
LP 2c	2.0
LP 1805	4.0

The results are shown in Figure 5, wherein it can be seen that the induction time increases as the degree of cross linking increases.

EXAMPLE 6

Tests similar to those of Example 5 were carried out using the following polymers having different chain lengths, to establish the relationship between molecular weight and induction time:

Liquid Polysulphide	n(formula I)
ZL 980	14
ZL 981	16
ZL 982	22
LP (OP1)	29

The results are shown in Figure 6.

It can be seen from Figure 6 that as the chain length increases the induction period also increases, from about 40 minutes up to 2 hours or more.

EXAMPLE 7 - Induction Period

Prior to making up stability trial samples an experiment was carried out to establish the induction time at different water addition levels for the particular materials being used. The results are shown in Fig.7. The formulations used in this trial are as outlined in 1 to 12 in Example 8 below, without the molecular sieve. A linear relationship between water content and induction time was found, as in Example 4.

EXAMPLE 8 - Stability

The following formulations were prepared to assess the stability of prereacted polysulphide polymers.

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<u>Test Number</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
LP32c	100	100	100	100	100	100	100	100
Calcium Peroxide	10	10	10	10	10	10	10	10
Water	0	0.5	0.5	1	1	1.5	1.5	1.5
Molecular Sieve (type 3A)	4	4	6	4	8	6	7	10

<u>Test Number</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
LP32c	100	100	100	100
Calcium Peroxide	10	10	10	10
Water	2	2	2	2
Molecular Sieve (type 3A)	4	7	10	12

In each system the molecular sieve was added 20 minutes before the end of the induction period as determined in Experiment 2.

Stability Trial Results

<u>Formulation No.</u>	<u>1.</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Viscosity initial Pa.S.	87.2	109	93	104	136	114
After 6 months ageing	203	203	105	203	cured	251
Time to Cure	-	-	-	13 days	-	13 days

<u>Formulation No.</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
Viscosity initial Pa.s.	124	152	169	131	152	147
After 6 months ageing	cured	324	cured	cured	cured	1046
Time to Cure	7 days	-	4 days	3 days	5 days	-

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It can be seen that it is possible to make a prereacted polysulphide that remains liquid for periods in excess of 6 months. The level of added water and subsequent addition of molecular sieve have a marked effect on stability. The experiment demonstrates that it is necessary to incorporate the effective absorption level of molecular sieve (20% by weight) on available water in order to render the system stable.

Example 9 - Effect of Temperature

Examples 1 - 8 were carried out at ambient temperature. To determine the effect of temperature on the preparation of prereacted polysulphides the following prereacted system was prepared

LP32c	100 pbw
calcium peroxide	10 "

and stored at different temperatures for 4 hours. It was found that peak instability was at 45°C. It was also unexpectantly found that at 60°C the prereacted system remained as stable as the sample at 25°C. Thus where it is not possible to make the prereaction at below 25°C, it is possible to make it at 60°C (Fig.8). In both cases, on exposure cure progressed immediately. The same conditioned at 60°C being slower than the sample at 25°C (Fig.9).

Example 10

Calcium Peroxide Paste for Prereaction

For ease of manufacture of the prereacted polysulphide, a paste of calcium peroxide with a plasticizer is used. The paste is easily dispersed in the liquid polymer. This

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removes the need to grind the polymer and the calcium peroxide powder together, which might bring about undesirable side reactions.

Three plasticizers were evaluated:

Santicizer 160 - butyl benzyl phthalate - Monsanto Ltd.

KMCC - trisopropyl naphthenate - Rutgers GmbH

Actrel 400 - aromatic substituted naphthenate -

Exxon Chemicals Ltd

After manufacture, the stability of the prereacted polymers based on these pastes was checked at 25°C and 60°C.

Plasticizer	Actrel 400		KMC		Santicizer 160	
Test temp.	25°	60°	25°	60°	25°	60°
Viscosity (poise)						
initial	547	510	483	483	510	494
7 days	765	617	684	567	557	540
49 days	1760	1130	1553	1035	713	666
100 days	1604	1121	1355	1137	529	542

The effect of the plasticizer on the cure activity with the prereacted polymer was checked by adding additional calcium peroxide and following viscosity increase. It was observed that the two naphthenate derivatives gave an acceleration to the rate of cure (for the sample stored at 25°C).

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Example 11

To demonstrate the effectiveness of the prereaction treatment of the liquid polysulphide in promoting faster cure, the following formulations were prepared.

	A.	B.
Prereacted LP	118	-
Untreated LP	-	118
Filler A	65	65
Pigment	20	20
Filler B	5	5
Filler C	110	110
Plasticizer	48	48
Adhesion promoter	1	1
Desiccant	5	5
Curing paste	17	17

The rates of skin formation at 25°C, 50% relative humidity (RH) were

	A.	B.
3 days	tack free	tacky
8 days	skin	tack free

The rates of skin formation outdoors (winter) were

	A.	B.
1 day	tack free	tack free
2 days	2mm skin	thin skin
5 days	3mm skin	1 mm skin
6 days	5mm skin	1.5 mm skin

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Example 12

Using the same formulation as Experiment 11, but with a level of calcium peroxide in the curing paste near to stoichiometry (with respect to liquid polysulphide) the following rates of cure were obtained (outdoors, winter).

	<u>with prereacted LP</u>	<u>with untreated LP</u>
1 day	skinned	tacky
3 days	2 mm skin	tacky
4 days	2 mm skin	tack free

Example 13

The effect of time of prereaction and type of prereaction were evaluated using the following resin systems:

	A.	B.	C.
LP-32c	100	100	100
Calcium peroxide	4	4	4
water	-	-	1.5
desiccant	-	-	8

System A was formulated immediately without prereaction; System B was allowed to prereact for 3 days before formulating; in system C the reaction was allowed to proceed for 4 hours before the desiccant was added to kill further reaction.

The resins were made into single component sealants using the formulation and cure pastes described in Example 10.

The relative rates of cure were then measured at 25°C, 50% RH.

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	A.	B.	C.
1 day	tacky	tacky	tack free
5 days	tacky	tack free	tack free
17 days	tack free	tack free	tack free

The relative rates of cure outdoors (winter) were - C fully cured in 1 day, B fully cured in 5 days and A fully cured in 7 days.

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CLAIMS

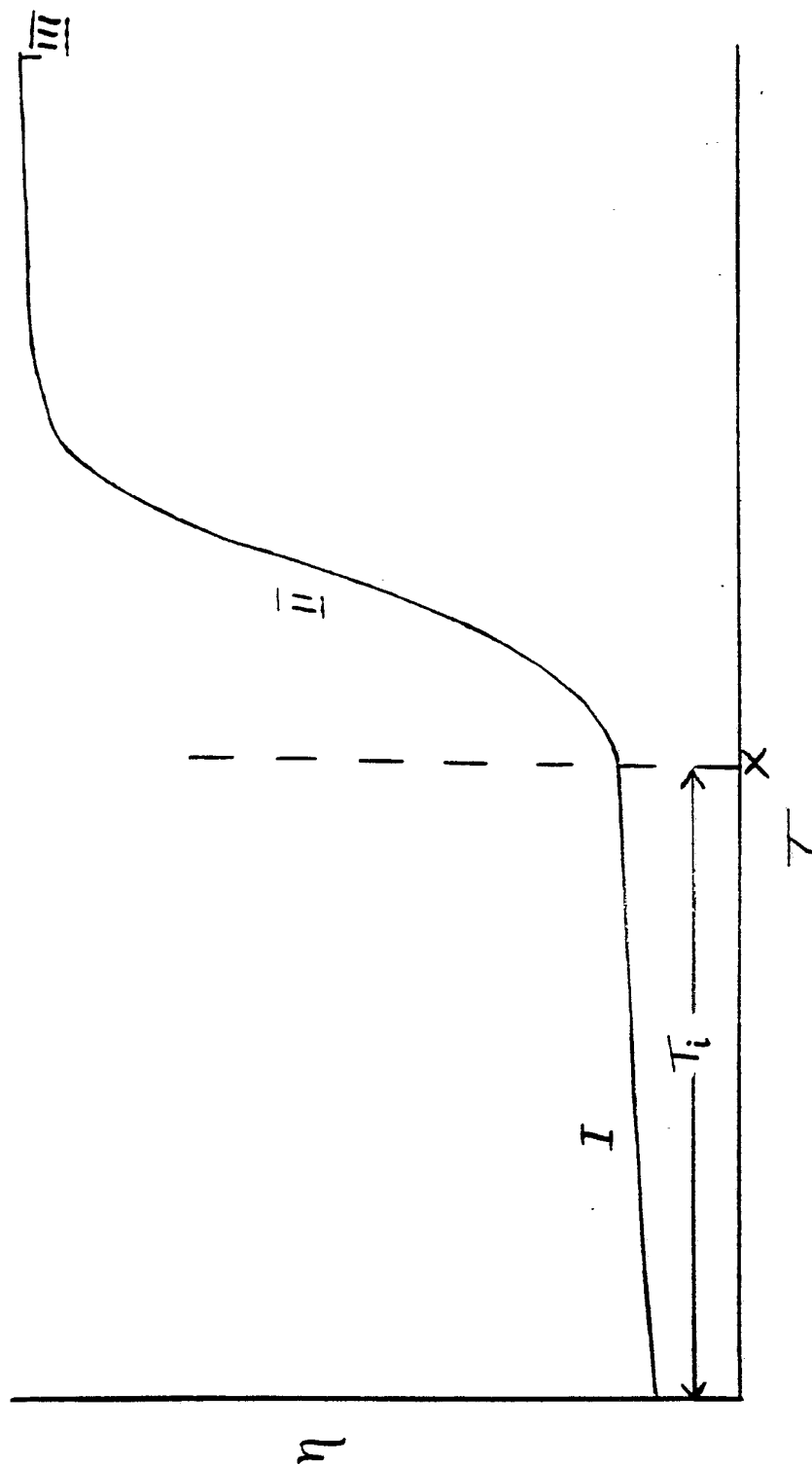
1. A method of making a polysulphide composition wherein a prepolymer having free mercaptan groups is mixed with a curing agent of a type activated by water, characterized in that the composition is subjected to a partial cure with water, the reaction then being stopped by dehydration.
2. A method according to claim 1, characterized in that the prepolymer is a liquid polysulphide having the general formula:
$$\text{HS}-(\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}_x)_n-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{SH}$$
 wherein x is from 2 to 5 and n is from 10 to 45.
3. A method according to claim 2, wherein the polysulphide has a branching level of 0 to 4%.
4. A method according to any preceding claim wherein the curing agent is an inorganic peroxide.
5. A method according to claim 4, wherein the curing agent is calcium or sodium peroxide.
6. A method according to any preceding claim wherein the amount of curing agent used is from 4 to 10 wt. parts per 100 wt. parts of the prepolymer.
7. A method according to any preceding claim, wherein the desiccant is a molecular sieve desiccant.
8. A method according to any preceding claim wherein a plasticizer is added to the system.

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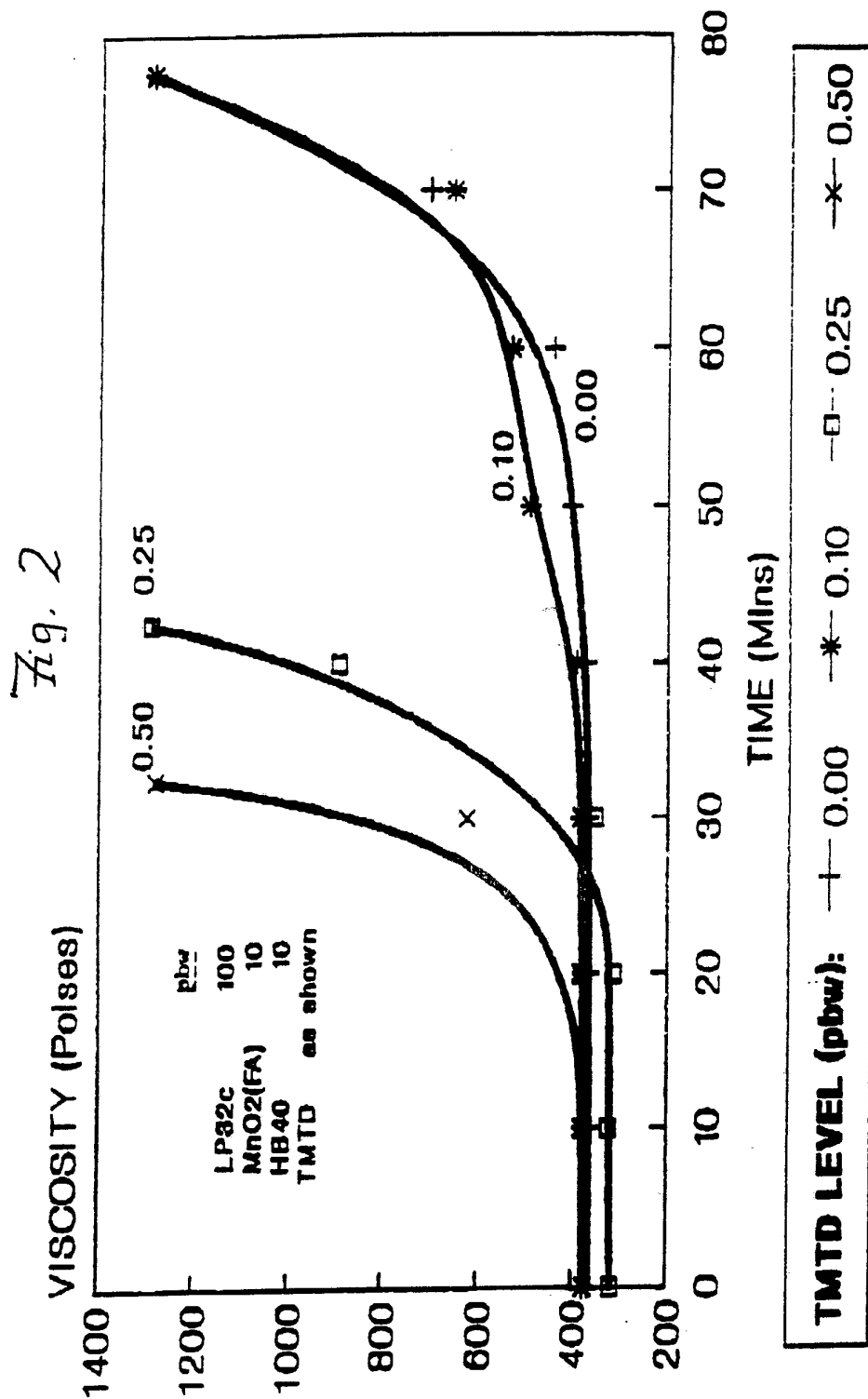
9. A method according to claim 8 wherein the plasticizer is added in the form of a paste with the curing agent.
10. A method according to any preceding claim wherein the partial cure is stopped at from 0 to 20 minutes before the end of the induction period, before the viscosity of the system rises.

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Fig. 1

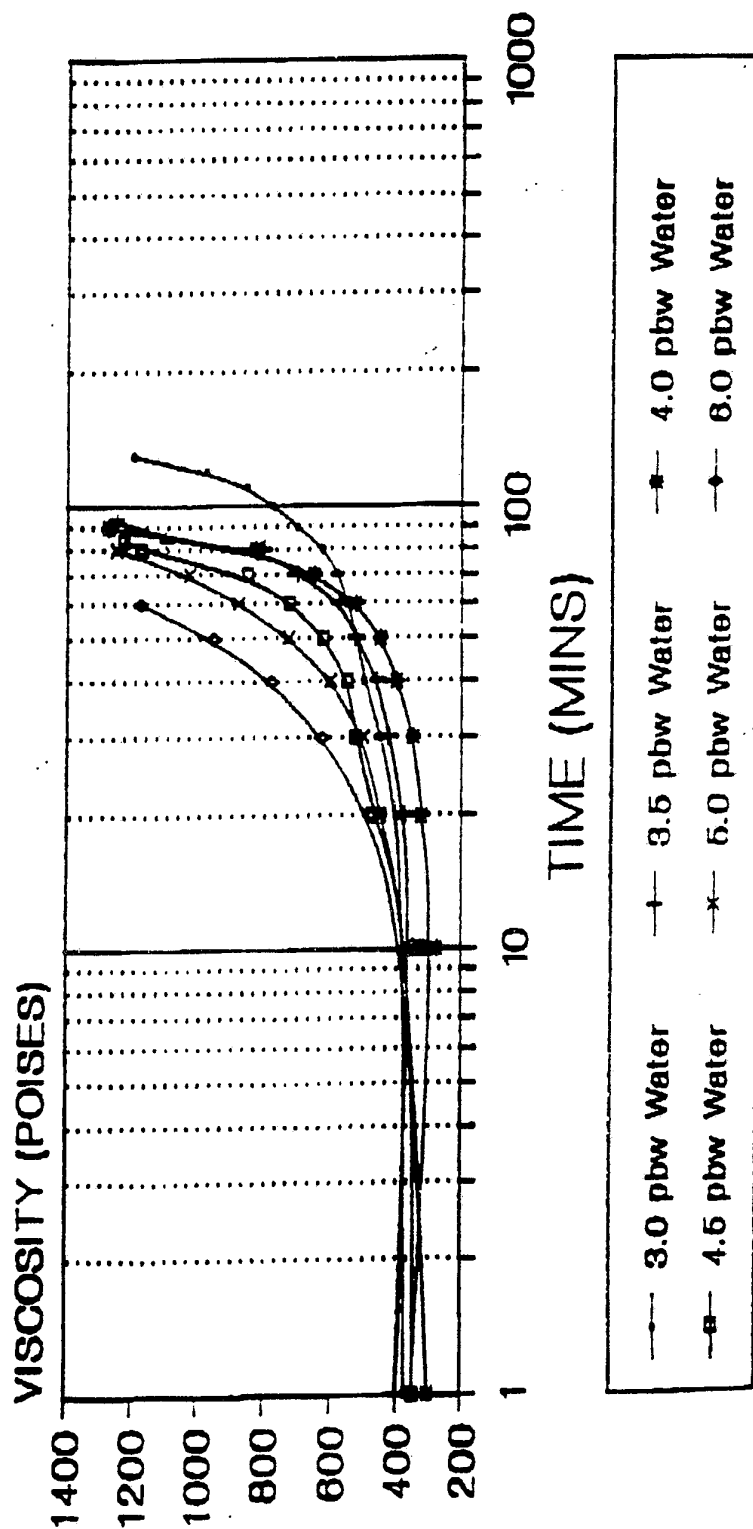


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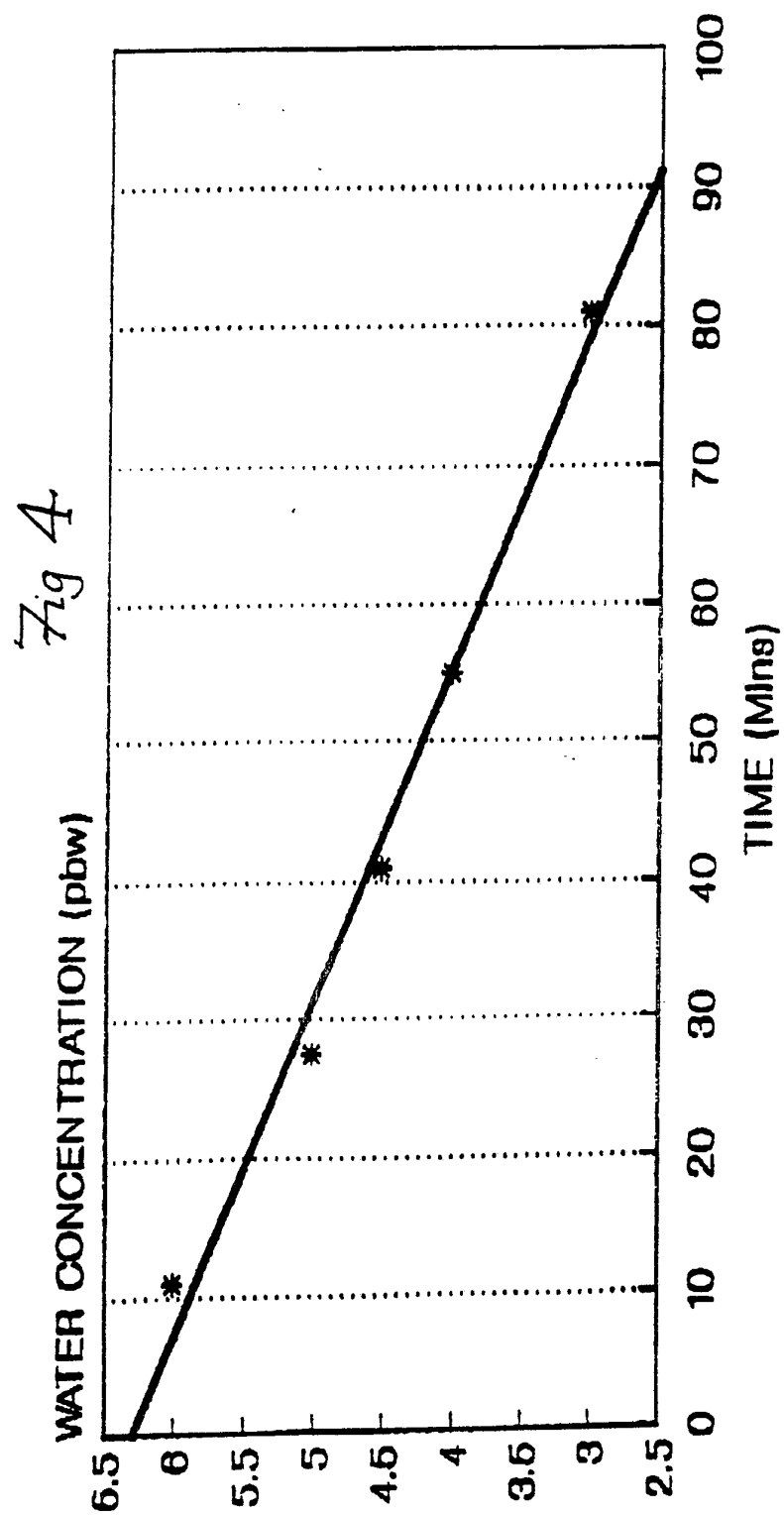


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Fig 3

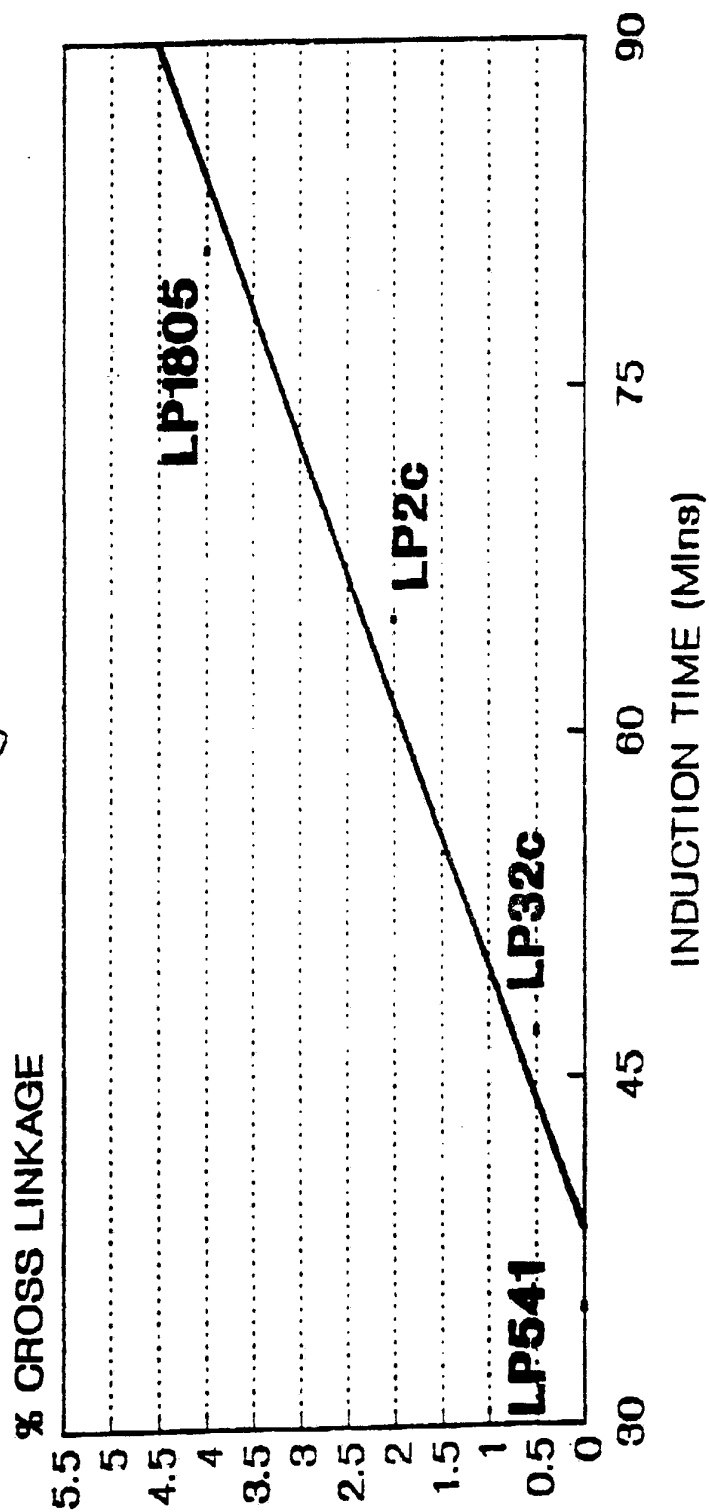


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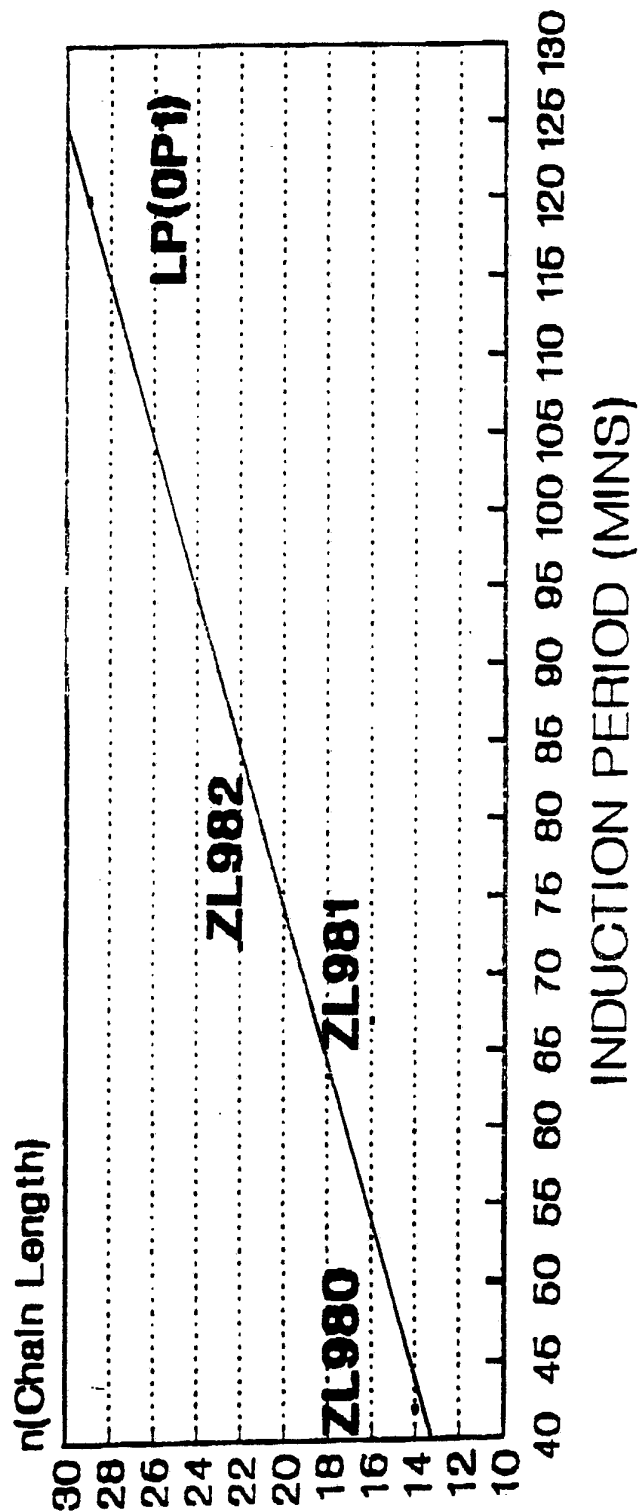
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Fig. 5



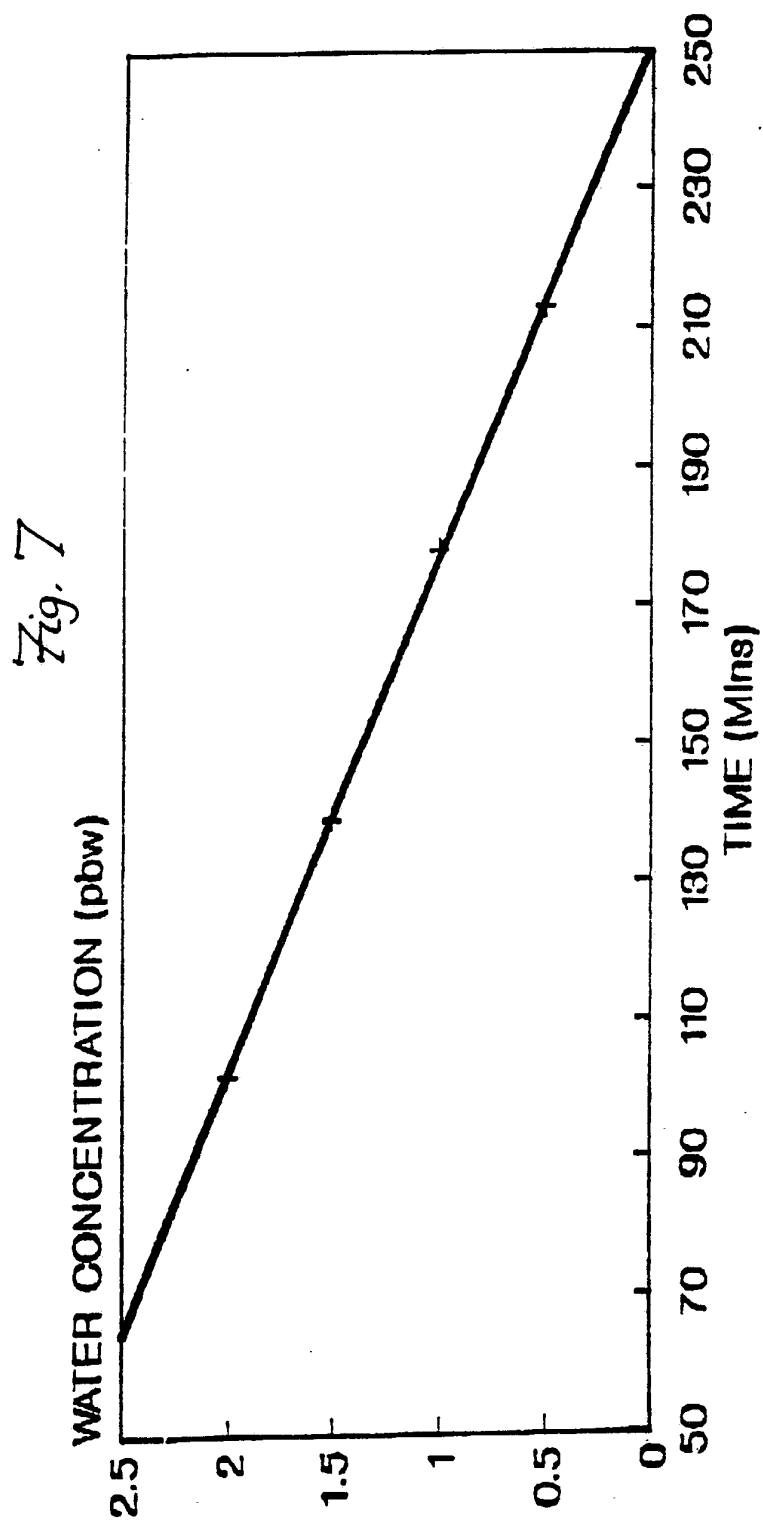
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Fig. 6



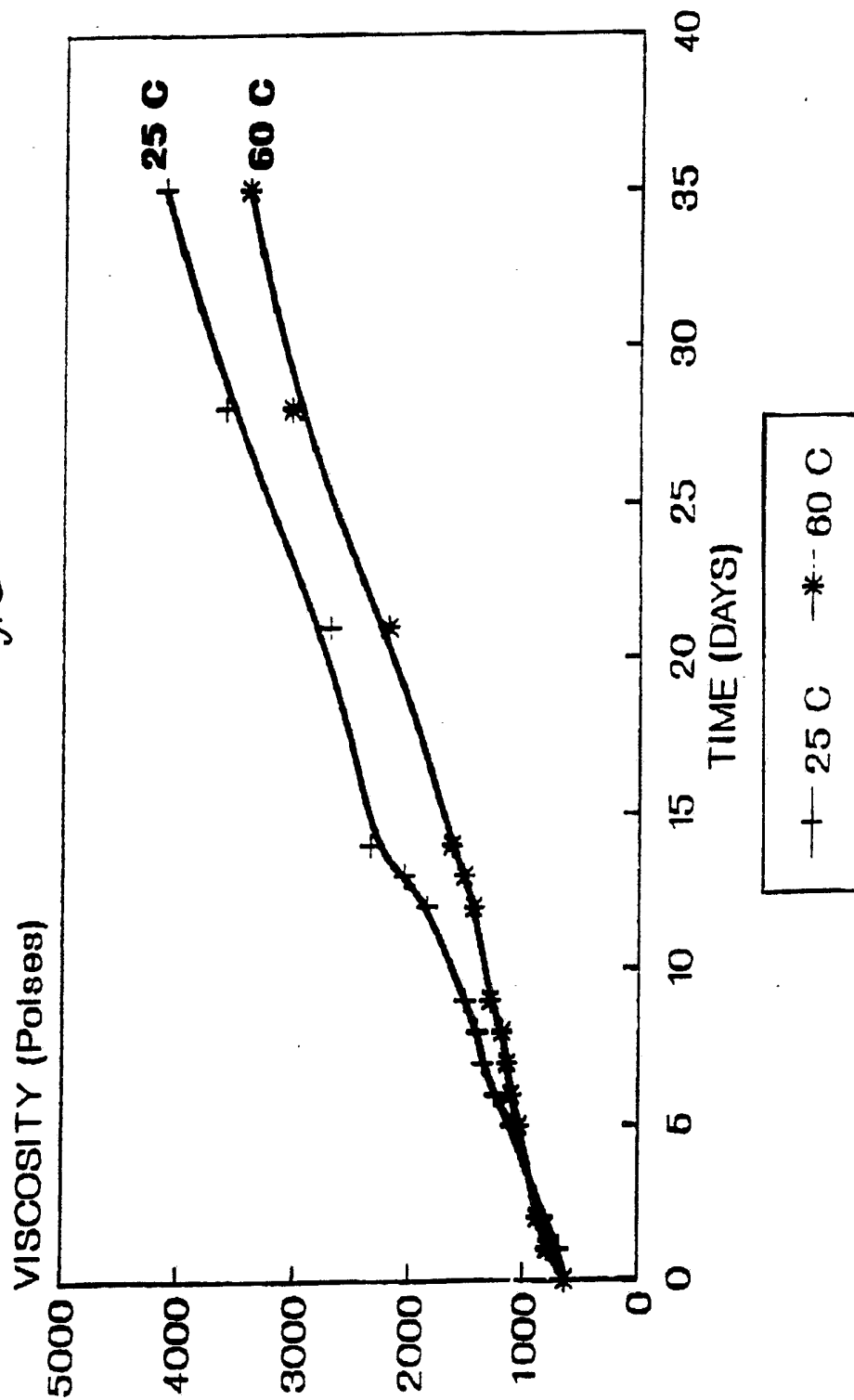
n - Number of Repeating Units / Chain Length

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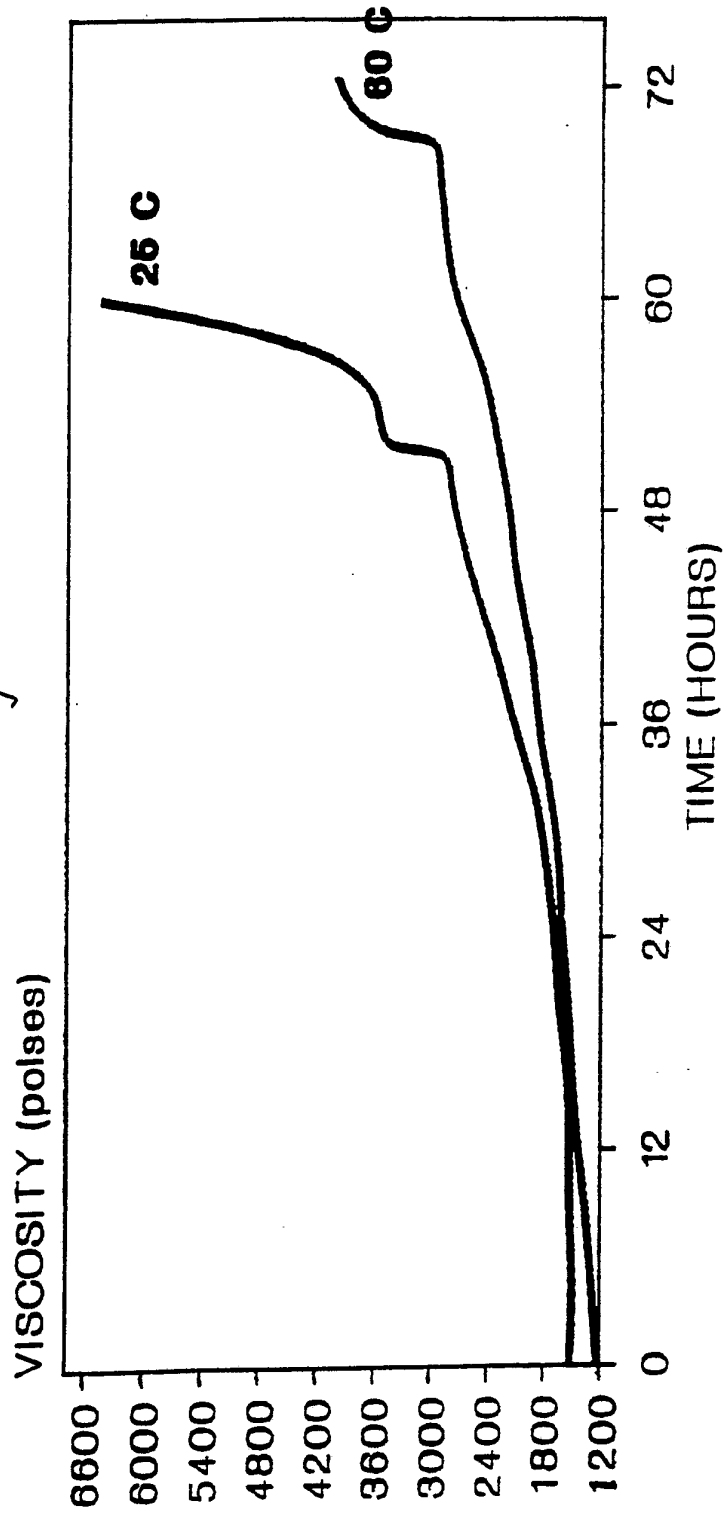
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Fig. 8



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Fig 9



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/00001

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 08 G 75/14		
II. FIELDS SEARCHED		
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Classification System	Classification Symbols	
IPC ⁵	C 08 G, C 08 L	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 3991039 (E. GUNTER et al.) 9 November 1976 see claims 1,2,9; examples VII,IX --	1-6
A	GB, A, 1158685 (THIOKOL) 16 July 1969 see claims; examples --	1-8
A	EP, A, 0153442 (PCI POLYCHEMIE) 4 September 1985 see claim 5 --	1
A	US, A, 3349047 (E. SHEARD) 24 October 1967 see claims 1,2 --	1
- / .		
<p>* Special categories of cited documents: ¹⁴</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
27th March 1990	65 35.00	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	MISS D. S. K. [Signature]	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Patent Abstracts of Japan, volume 7, no. 248 (C-193)(1393), 4 November 1983 & JP, A, 58134123 (TOURE CHIOKOORU K.K.) 10 August 1983 --	1
A	Chemical Abstracts, volume 76, no. 20, 15 May 1972, (Columbus, Ohio, US), see abstract no. 114535c & JP, A, 7101264 (KANEGAFUCHI SPINNING) 13 January 1971 --	1
A,P	EP, A, 0332754 (RÜTGERSWERKE) 20 September 1989 see claim 7 -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9000001
SA 33516

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 11/05/90
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3991039	09-11-76	None	
GB-A- 1158685	16-07-69	BE-A- 702467	09-02-68
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