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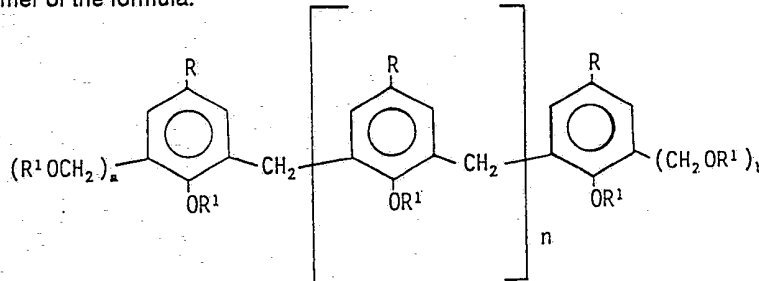
C3P

Selected US specifications from IPC sub-class

C08F

(54) Cyanoacrylate adhesive compositions

(57) Instant adhesive compositions, particularly alpha-cyanoacrylate compositions, contain as accelerator an acyclic phenol-formaldehyde oligomer of the formula:



wherein  $n = 0 - 10$ ,

$R^1 = CH_2C(O)R^2$ , or H, or  $-CH_2COOH$ , at least 50% of the  $R^1$  groups being  $-CH_2C(O)R^2$ ,

$R^2 =$  hydrocarbyl, aryl, hydrocarbylaryl, hydrocarbyloxy, aryloxy, hydrocarbylaryloxy and substituted derivatives thereof,

$R =$  hydrogen, halogen, hydrocarbyl, aryl, hydrocarbylaryl, and  $a=1, b=0$ ; or  $a=b=0$ ; or  $a=b=1$ .

"INSTANT ADHESIVE COMPOSITIONS UTILIZING FUNCTIONALISED PHENOL-FORMALDEHYDE OLIGOMERS AS ACCELERATORS; AND PREPARATION OF SUCH OLIGOMERS"

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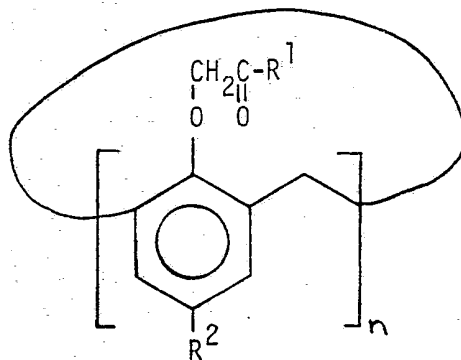
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This invention relates to instant adhesive compositions, particularly cyanoacrylate compositions, which contain certain functionalised acyclic phenol-formaldehyde oligomers as accelerators. The invention also relates to the preparation of such oligomers.

US Patent 4 556 700 Harris et al describes the use in cyanoacrylate adhesive compositions of calixarene compounds represented by the formula:

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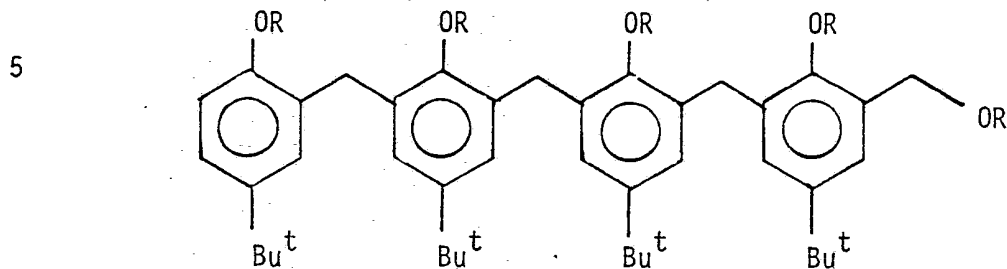
where R<sup>1</sup> is alkyl, alkoxy, substituted alkyl or substituted alkoxy; R<sup>2</sup> is H or alkyl; and n = 4, 6 or 8.

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Calixarenes are macrocyclic phenol-formaldehyde condensation oligomers. The synthesis of calixarenes is described in C. Gutsche, Acc. Chem. Res., 16, 161-170 (1983). Gutsche at pages 15163, 164 and 165 reports the formation as intermediate compounds of acyclic phenol-formaldehyde oligomers which are cyclised to produce the calixarenes.

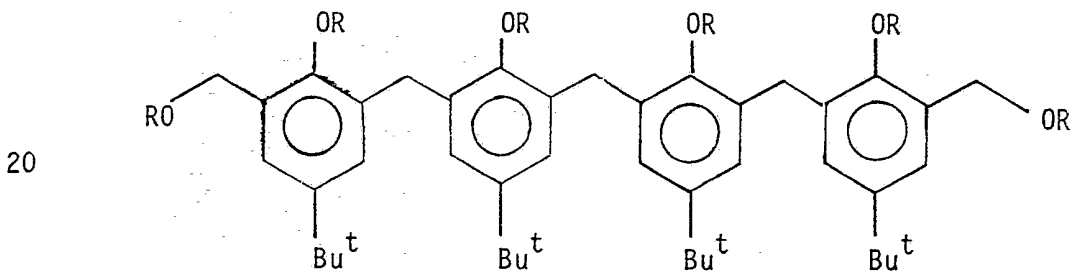
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McKervey et al., Chem.Soc., Chem. Commun., 1985, 388 refer to an acyclic pentaester of the formula:



wherein  $R = \text{CH}_2\text{CO}_2\text{Et}$ , now believed by the present inventors to have been the hexaester:

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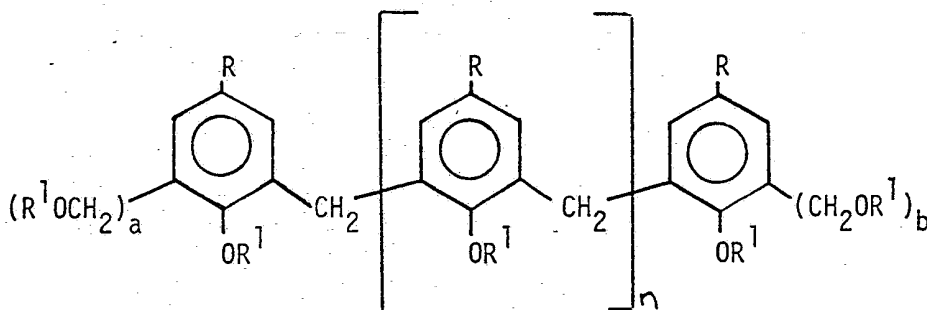


25 This compound is shown to have a very low level of phase transfer affinity for alkali metal cations, in contrast to the analogous calixarene esters (see Table 1).

30 It has hitherto been assumed that the ion transport properties of calixarenes, and their activity as accelerators in cyanoacrylate adhesive compositions, were dependent upon their macrocyclic structure.

35 However we have now surprisingly found that certain functionalised acyclic phenol-formaldehyde oligomers are useful as accelerators in cyanoacrylate adhesive compositions.

The present invention therefore provides an alpha-cyanoacrylate adhesive composition containing as accelerator an acyclic phenol-formaldehyde oligomer of the formula:



15 wherein  $n = 0 - 10$ ,

$R^1 = CH_2C(O)R^2$ , or H, or  $-CH_2COOH$ , at least 50% of the  $R^1$  groups being  $-CH_2C(O)R^2$ ,

20  $R^2 =$  hydrocarbyl, aryl, hydrocarbylaryl, hydrocarbyloxy, aryloxy, hydrocarbylaryloxy and substituted derivatives thereof,

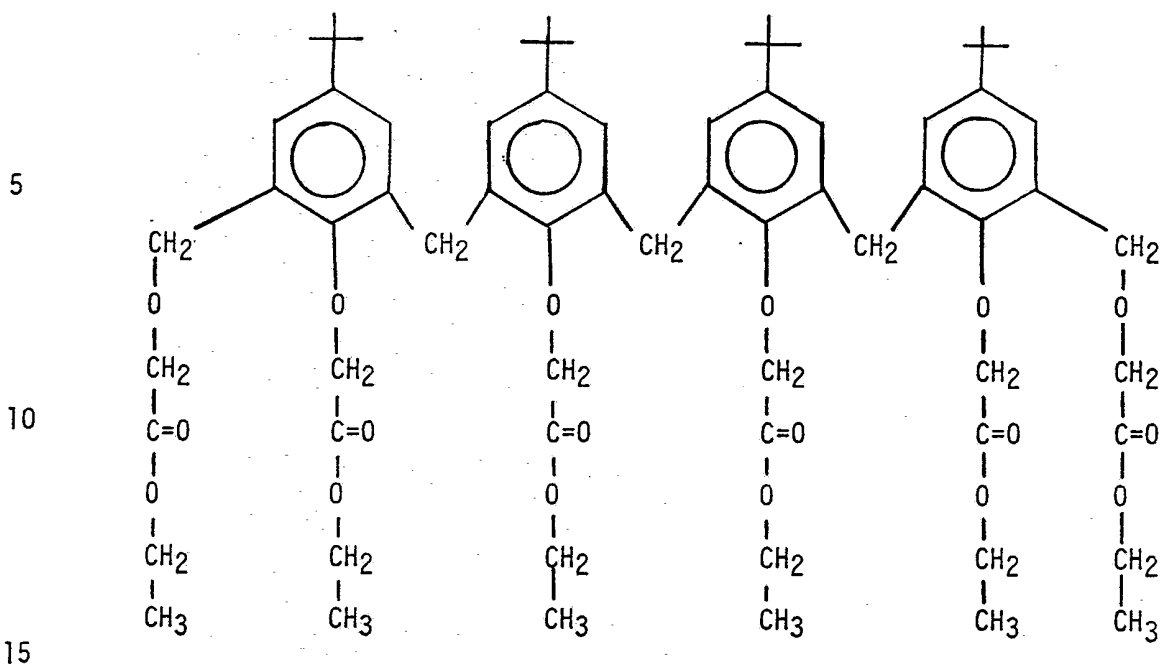
$R =$  hydrogen, halogen, hydrocarbyl, aryl, hydrocarbylaryl, and  $a=1, b=0$ ; or  $a=b=0$ ; or  $a=b=1$ .

25 Preferably 100% of the  $R^1$  groups are  $-CH_2C(O)R^2$ .

In the above formula, hydrocarbyl is suitably alkyl or alkenyl, especially having 1-10 carbon atoms, more particularly 1-5 carbon atoms. If  $R^2$  is a substituted derivative, it may suitably be substituted with one or more halo groups or substituted or interrupted by one or more oxo groups. Halogen may suitably be chlorine, fluorine, bromine or iodine. Aryl preferably has 6-20 carbon atoms, more especially 6-10 carbon atoms.

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35 A particularly preferred acyclic oligomer is of the formula:



The acyclic oligomers may be prepared by the routes described as preliminary steps in the synthesis of cyclic oligomers in C. Gutsche, Acc. Chem. Res. 1983, 16, 161-170 or in B. Dhawan and C. Gutsche, J. Org. Chem. 1983, 48, 1536-1539, particularly at page 1538, followed by substitution of appropriate side chains to form partly or fully etherified oligomers. The halogenated oligomers may be prepared by the routes described in Helvetica Chimica Acta, Vol. 64. Fasc. 2 (1981)-Nr. 59 P 599 or in Helvetica Chimica Acta. - Vol. 65. Fasc. 4 (1982)-Nr. 113 P 1221 again followed by substitution of appropriate side chains to form partly or fully etherified oligomers.

The present invention provides new cyanoacrylate compositions for bonding wood and other de-activating surfaces such as paper, leather, ceramic, plastics and metals with chromate treated or acidic oxide surfaces. The inventive compositions are standard cyanoacrylate adhesive formulations to which have been added as accelerators, acyclic phenol-formaldehyde oligomers as defined above. The acyclic oligomers are employed in amounts conventional for cyanoacrylate accelerators, preferably at levels between about 0.1% and 2% by weight of the composition.

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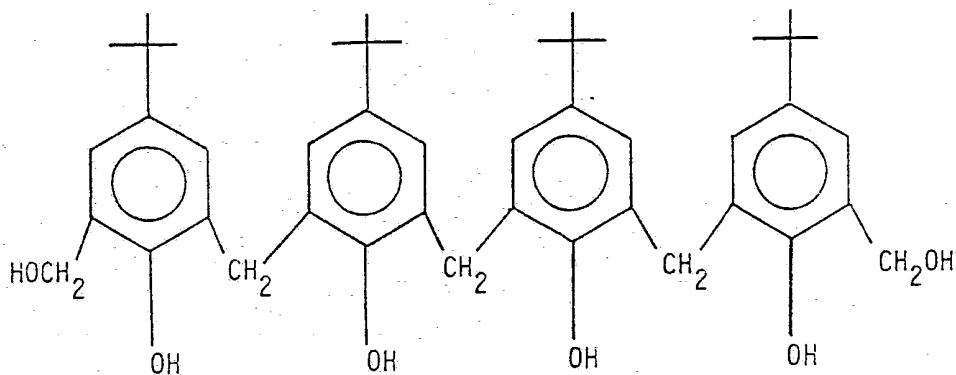
The standard cyanoacrylate compositions are as described in US Patent 4 556

700 Harris et al at column 2 line 18 - column 3 line 32, the contents of which are incorporated herein by reference.

The invention may be further understood with reference to the following non-limiting examples:

#### Example 1 Preparation

Following the Cornforth Procedure\* 10.0g (0.066 mole) p-t-butylphenol was mixed with 10 mls 3N aqueous NaOH and 9.7g of 37% aqueous formaldehyde solution. The mixture was heated at 50-55°C for 45 hours and then at 110-120°C for 2 hr to give an off white solid. This solid was stirred with 100 ml 1N HCl for 1 hour to neutralise the base filtered and the solid washed with water to give after drying in a 110-120°C oven for 1 hour 10.8 g (94% yield) of off-white oligomer powder;

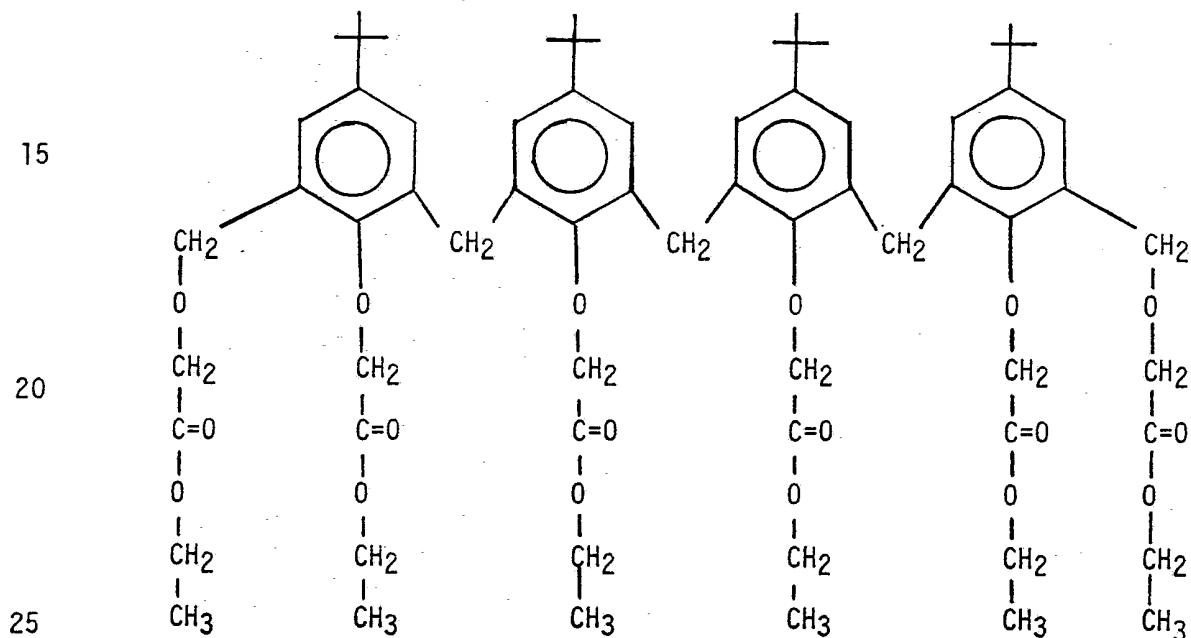


\*reference for Cornforth Procedure: Brit J. Pharmacol 10, p73, 1955 by J.W. Cornforth, P.D'Arcy Hart, G.A. Nicholls, R.J.W. Rees and J.A. Stock.

#### Example 2.

6.5 g (0.0094 mole) tetrameric open chain oligomer prepared as in Example 1 was mixed with 13.4 g (0.080 mole) ethyl bromoacetate, 8.3g (0.060 mole) powdered anhydrous potassium carbonate and 100 mls dry

analar acetone and the whole was refluxed with stirring under nitrogen for 72 hours. After this time the reaction mixture was cooled to room temperature and solids were filtered off. The volatiles were removed from the filtrate at reduced pressure to give 7.2 g of heavy pale yellow oil which was taken up in dichloromethane which was washed twice with 10% aqueous HCl and four times with water. The dichloromethane solution was then dried over dried magnesium sulphate and the volatiles were removed to give 6.9 g pale yellow oil product which was chromatographed on a neutral alumina column using dichloromethane as eluent. Removal of volatiles gave a colourless solid product m.pt. 67-68.5°C identified as the etherified product:



by infra red spectroscopy and elemental analysis

i.r. spectroscopy results: 1750 (S)C=O

Elemental Analysis results : (Calc'd for C<sub>69</sub>H<sub>96</sub>O<sub>18</sub>  
C:68.29, H:7.97, Found C:67.51, H:7.93).

### Example 3.

Ethyl cyanoacrylate stabilised with 10 ppm BF<sub>3</sub> was used as a base adhesive formulation. The additive shown below was dissolved in base adhesive at the indicated level and fixture times on copy paper and white deal were determined. The result below demonstrates the good

accelerative activity for the functionalised acyclic oligomer:-

TABLE

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Additive	Amount	<u>Fixture Time</u>	
		Copy Paper	White Deal
None	-	60 seconds	5-6 minutes
Example 2 Product.	0.5%	30-40 seconds	30-40 seconds

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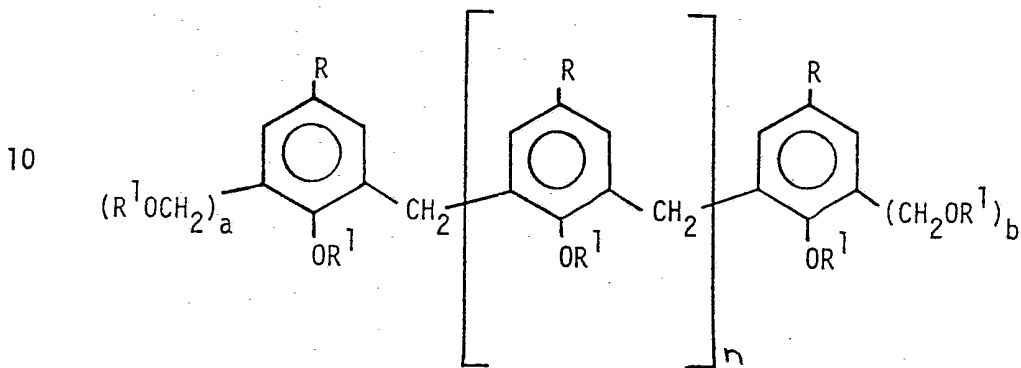
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CLAIMS

1. A cyanoacrylate adhesive composition containing as accelerator an acyclic phenol-formaldehyde oligomer of the formula:



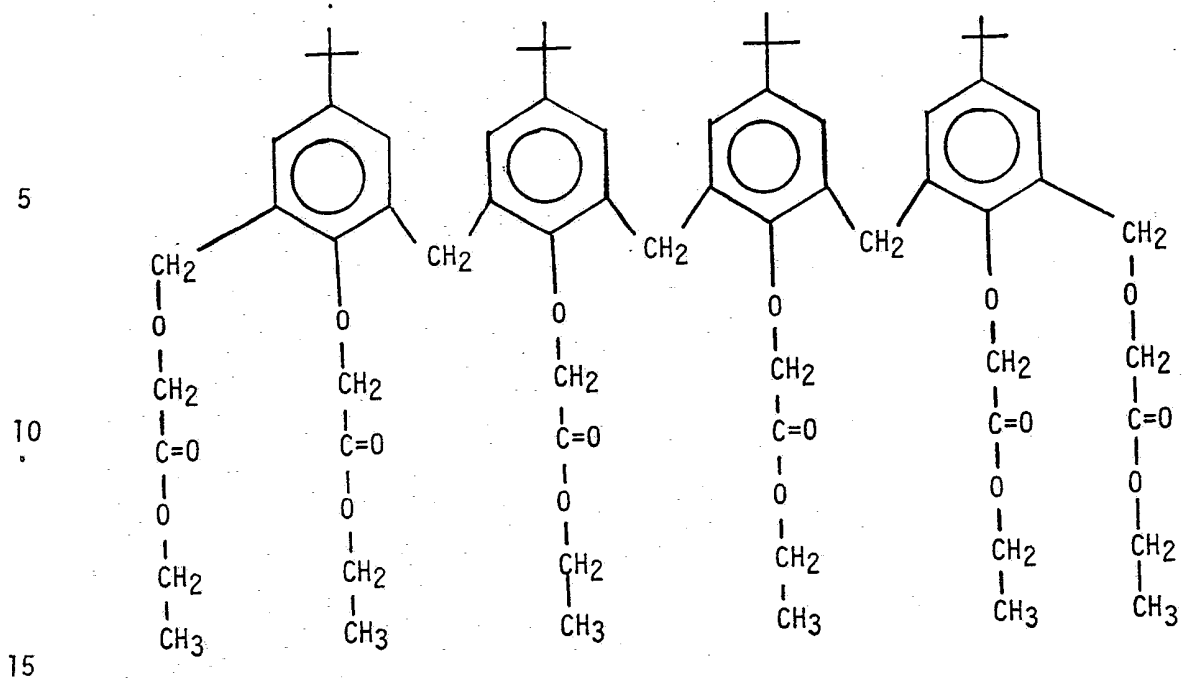
wherein  $n = 0 - 10$ ,

$R^1 = \text{CH}_2\text{C}(\text{O})\text{R}^2$ , or H or  $-\text{CH}_2\text{COOH}$ , at least 50% of  $R^1$  groups being  $-\text{CH}_2\text{C}(\text{O})\text{R}^2$ ,

$R^2 =$  hydrocarbyl, aryl, hydrocarbylaryl, hydrocarbyloxy, aryloxy, hydrocarbylaryloxy and substituted derivatives thereof,

$R =$  hydrogen, halogen, hydrocarbyl, aryl, hydrocarbylaryl, and  $a=1, b=0$ ; or  $a=b=0$ ; or  $a=b=1$ .

2. A composition according to claim 1 wherein  $R^1$  is  $\text{CH}_2\text{C}(\text{O})\text{R}^2$ .
3. A composition according to claim 1 or 2 wherein hydrocarbyl is alkyl or alkenyl having 1-10 carbon atoms.
4. A composition according to claim 3 wherein hydrocarbyl is alkyl or alkenyl having 1-5 carbon atoms.
5. A composition according to any of the preceding claims wherein the acyclic oligomer is of the formula:



6. A composition according to any of the preceding claims wherein the acyclic oligomer is employed at levels between about 0.1% and 2% by weight of the composition.

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