follows the Huggins equation,

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c$$

with $k_H = 2.9 \pm 0.2$. Also, the inherent viscosity, $(\ln\eta_r)/c$, follows the Kraemer equation,

$$(\ln\eta_r)/c = [\eta] + k_K[\eta]^2c$$

with $k_K = 2.15 \pm 0.15$.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support of the Comisión de Investigaciones Cientificas de la Provincia de Buenos Aires, Argentina.

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Phenolic resins for oil varnishes: 2. Simple method of giving reactivity to oil-non-reactive resins

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(Received 9 January 1979; revised 21 June 1979)

A modified oil–resin was prepared according to the following formulation (in parts by weight): *p*-tert-butylphenol novolac ($\bar{M}_n$ = 650, preparation described elsewhere[1]) = 40, tung oil = 40, polymerized linseed oil (200 poise at 20°C) = 20, hexamethylenetetramine = 0 to 6. The reactor was a one and a half litre stainless steel vessel, provided with an anchor impeller and jacketed with temperature controlled electrical heating system. A vertical condenser and a Fe–constantan thermocouple entering the reaction mixture were attached to the cover. Sampling and final discharge were carried out by means of a valve placed at the bottom.

The resin and the oil mixture were charged to the reactor and temperature was increased to a constant value (in the range 200 to 300°C) which was arbitrarily taken as the zero polymerization time (the reaction was so slow that this assumption was considered satisfactory). At this stage, the selected amount of hexa was added and the reaction taken to a point where a 1:1 wt/wt solution of the mixture in white spirit gave a viscosity of 200 to 300 cp at 20°C.

The varnish was formulated with the addition of white spirit in a weight ratio 1:1, cobalt and lead in proportions varying from 0.03%to 1% and 0.25% to 1%, respectively, with respect to total oil. These two metals were added as solutions of the corresponding octoates in white spirit.

Table 1 shows the drastic reduction in gel time resulting from the addition of hexa to the novolac, the tung oil, and their mixtures. Further, the effect on both reactants was similar, implying that a copolymerization could take place. This is important in view of the fact that when the phenolic resin acts as a mere filler of the polymerized oil, properties of the varnish film are less satisfactory[2].

The result of varying the hexa concentration is shown in *Figure 1.* A minimum in the gel time at 255°C is observed, corresponding to a hexa concentration of 5% with respect to total oil (3 parts in the formulation). At this concentration the effect of temperature was studied, giving the results plotted in *Figure 2.* At temperatures close to 300°C the gelation was almost instantaneous.

The N content of the final varnish was determined by the Kjeldahl method. It was found that the sample prepared with 5% hexa had a residual nitrogen content of only 3.3% of that added, the major part being evolved as ammonia during polymerization.

Thus, the slow process of making varnishes from oil–nonreactive novolacs may be substantially accelerated by adding suitable amounts of hexamethylenetetramine. Its effect may be visualized by returning to the observations of Hultzsch, and Cunnen, Farmer and Koch[3], supporting the presence of chromane derivatives in the reaction between

Table 1

	1	2	3	4	5
Novolac	–	100	40	–	40
Tung oil	100	–	40	–	40
Linseed oil	–	–	20	100	20
Hexa	10	15	6	10	–
Gel time at 250°C (min)	18	16	17	–	300

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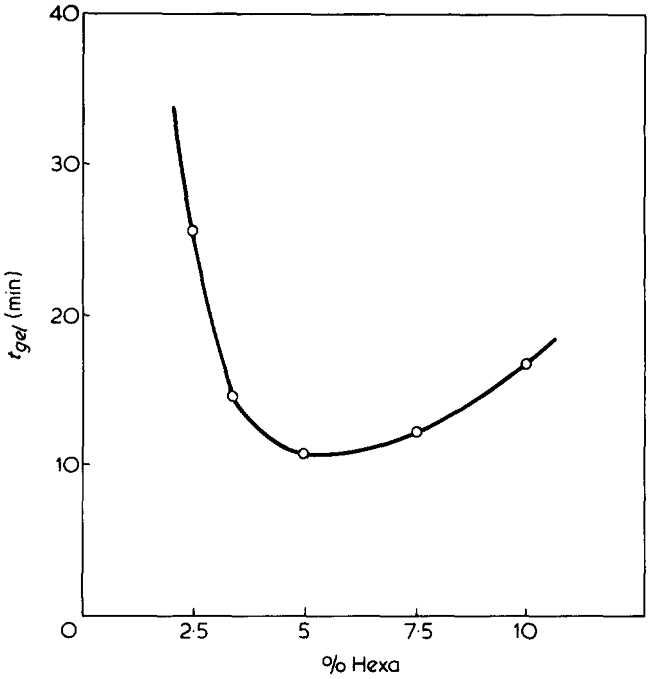
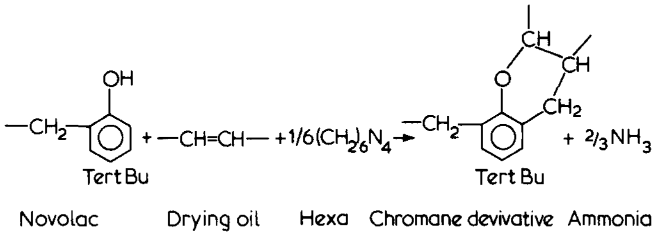


Figure 1 Gel time of the novolac–drying oil mixture as a function of the % hexamethylenetetramine/total oil at 255°C

oil-reactive novolacs and unsaturated compounds. In our case, the following stoichiometry can be proposed:



The reaction scheme must of course be completed taking into account the individual novolac and drying oil gelations resulting from the hexa addition. However, if these reactions are neglected in a first estimation, the minimum amount of hexa which is necessary to gel the system may be calculated as follows.

The novolac functionality is $f_N = 2$, the tung oil functionality is $f_T = 8.2$ (average number of double bonds on the basis of 88% eleostearic acid, 6% oleic acid, 4% estearic acid and 2% linoleic acid), the hexa functionality is $f_H = 6$ and the initial molar ratio of novolac to tung oil is $N_0/T_0 = 1.344$. The tung oil conversion at the gel point is given by[4]

$$p_{T,gel} = \left\{\frac{f_N N_0}{f_T T_0 (f_N - 1)(f_T - 1)}\right\}^{1/2} = 0.213$$

The corresponding novolac conversion is

$$p_{N,gel} = \frac{f_T T_0}{f_N N_0}\, p_{T,\text{gel}} = 0.650$$

Table 2

Sample	% Hexa/ Total oil	Polymerization conditions	Microhardness Vickers Units
40 Novolac, 40 Tung oil, 20 Linseed oil, 100 White spirit, 1%Co/oil	–	T = 250°C, t = 4 h	54
	1	T = 250°C, t = 2 h	45
	5	T = 220°C, 10 min	43
Commercial	–	Unknown	35

Table 3

% Cobalt/oil	% Lead/oil	Microhardness Vickers Units
1 .0	–	54
0.2	1	25
0.1	0.9	11
0.05	0.25	9
0.03	0.27	4

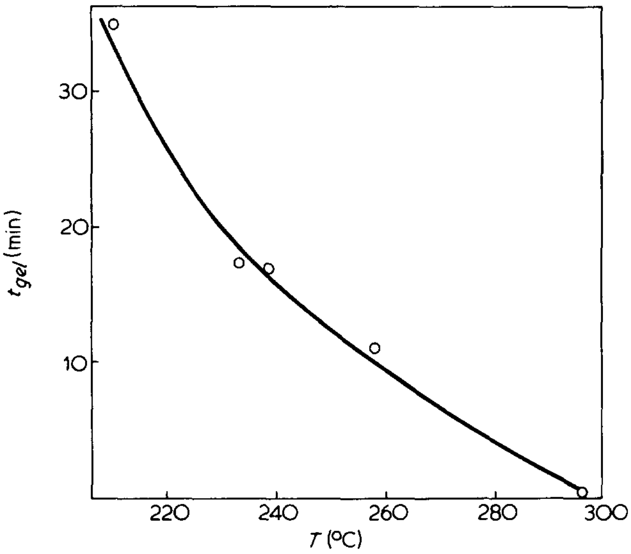


Figure 2 Gel time of the novolac–drying oil–hexamethylenetetramine (5% with respect to total oil) mixture as a function of temperature

and the minimum amount of hexa to be added follows from

$$f_H H_{0,gel} = f_N N_0 p_{N,gel} = f_T T_0 p_{T,gel}$$

resulting in

$$H_{0,gel}/T_0 = 0.291 \text{ or } \% \text{ Hexa/Total oil} = 3.1$$

The last value lies in the experimental range. On the other hand, the increase in the gelation time after the minimum (*Figure 1*) may result from the dilution effect of further hexa additions.

The Vickers microhardnesses (Duromet, Leitz) of varnish films applied on glass surfaces, after a three-week exposure at ambient conditions, are shown in *Table 2*. A commercial marine varnish was used for comparison purposes. All the values are in the same range, although the addition of hexa leads to a slight hardness decrease.

The chemical resistance of the different films was measured with accelerated conventional tests. It was found that the properties of varnishes prepared with or without hexa were similar. They appear to be superior to those of the corresponding commercial films.

A wide range of suggested driers concentrations was found in related literature. *Table 3* shows the effect of several driers proportions on the hardness of films. Not only was the film hardness severely diminished when decreasing the Co amount, but also the drying time was greatly increased. Further, lead was found to be inconvenient for an adequate gloss retention. Thus, for our particular case it is recommended to use 1% Co, giving a 'print free' drying time of two hours.

In conclusion, an excellent varnish may be obtained by heating 40 parts of a novolac ($\bar{M}_n$ = 560), 40 parts of tung oil, 20 parts of polymerized linseed oil (200 poise at 20°C) and 3 parts of hexamethylenetetramine, for 10 minutes at 220°C, thinning with white spirit in a 1:1 weight ratio and adding 1% Co with respect to total oil.

Acknowledgement

We gratefully acknowledge the financial support of the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Argentina.

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Polymeric systems for acoustic damping: 2. Preparation and properties of a poly(vinyl isobutyl ether)—poly(methyl acrylate) interpenetrating polymer networks

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Introduction

Interpenetrating polymer networks (IPN) constitute a class of materials in which two usually distinct networks are intimately combined. There are a variety of synthesis methods[1–5], but broadly speaking a three-dimensional network of the first component is established in the presence of the monomer plus crosslinking agent of the second component which is then polymerized also to give a three-dimensional network. A number of recent reviews[6–8] of various aspects of these materials are available.

The majority of IPN's exhibit phase separation, but the size, shape and extent of connectivity of the phases can be varied considerably by altering the mutual compatibility of the constituent polymers[9], the crosslink density – particularly of the first formed network[10], the synthesis method[5,11] and the composition[4,11].

An IPN formed by swelling crosslinked polyvinyl isobutyl ether sheet in methyl acrylate containing a crosslinking agent, and then polymerizing this monomer, has been investigated using, principally, dynamic mechanical spectroscopy. In an earlier paper[12] reference was made to the suitability of such materials for acoustic damping. It is believed that this material has interesting properties from this point of view.

Experimental

Polyvinyl isobutyl ether (Lutonal ICK) was kindly donated by B.A.S.F., while the methyl acrylate and divinyl benzene were supplied by Cambrian Chemicals. *Table 1* has characterization data for the uncrosslinked polyvinyl isobutyl ether. Crosslinked sheets of polyvinyl isobutyl ether were prepared by milling the polymer on an unheated Farrell two-roll mill and then adding 2.5 g of the crosslinking agent, tertiary butyl peroctoate, per 100 g of polymer. After this addition milling was continued for a further 10 min. Sheets were then cured in a hot press at 120°C for 30 min.

Sheet samples were swollen in methyl acrylate containing 1% by wt of divinyl benzene as crosslinking agent and 0.2% by wt of initiator (AIBN) to give a final composition of

Table 1 Characterization data for the uncrosslinked polyvinyl isobutyl ether

$\bar{M}_n \times 10^{-3}$ [a]	282
$\bar{M}_w/\bar{M}_n$ [b]	1.86

[a] Membrane osmometry. Toluene at 37°C
[b] Gel permeation chromatography. Chloroform as solvent

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