

NOTE

Reaction of Unsaturated Linseed Oil with a Timber Constituent

INTRODUCTION

Linseed oil and alkyd resins derived from it are used extensively as surface finishes to embellish and protect timber. The presence of unsaturations in linseed oil and in alkyds indicate that the possibility of cross-linking between the finish and the unsaturated sites of polymeric wood constituents does exist. Raw linseed oil was reacted under various conditions with guaiacol and with β -methylstyrene as simple model compounds of reactive wood lignin moieties. The apparent rate constants of the total reaction were calculated and compared.

EXPERIMENTAL

Raw (not boiled) linseed oil, 2.9 g, in 1.8 g xylene was reacted at 50, 70, 80, and 100°C for 3 h. Identical amounts of linseed oil were reacted under identical conditions with 1.5, 3.0, and 5.0 g of β -methylstyrene or with equivalent molar amounts of guaiacol.

An identical amount of linseed oil alone and linseed oil with 3.0 g of β -methylstyrene were reacted at ambient temperature (25°C) under UV irradiation for 3 h or, alternatively, by addition of 1% cobalt naphthenate and 1% of methyl ethyl ketone peroxide (MEKP) at 50°C for 3 h. Samples were taken at 0.5 h intervals. The progress of the reaction of the linseed oil alone was followed from the area variation of the infrared (IR) bands at 780 and 760 cm^{-1} ; the former due to unconjugated carbon-carbon double bonds, and the latter, to conjugated carbon-carbon double bonds in the unsaturated fatty acids triglycerides contained in the linseed oil. Added to these, the variation of the peak at 1490 cm^{-1} due to free styrene was also considered for the linseed oil/styrene reaction.¹ The areas of both the 780 and 1490 cm^{-1} IR bands decreases with increase of the time of reaction. The reaction of linseed oil and guaiacol was followed from the variation of the area of the IR bands at 780 cm^{-1} , the latter being due to the increasing appearance of 1,2,4-trisubstituted benzene rings due to the attack of the unsaturated fatty acids on to the guaiacol ring with progress of the reaction with time.¹ The variation of the IR bands for all the reactions was followed

continuously during the periods of reaction indicated. The second-order rate constant was calculated by equating the variations of the bands at 780, 760, and 1490 cm^{-1} with the original and final concentrations of, respectively, the unconjugated and conjugated carbon-carbon double bonds of β -methylstyrene as already reported.¹ The same procedure was followed with the IR band at 900 cm^{-1} for the appearance of 1,3,4-trisubstituted benzene rings related to the initial and final concentration of guaiacol (disubstituted benzene nuclei). The UV light intensity used for the UV-initiated reaction was a Camag universal UV lamp, 50 Hz used at 254 nm.

DISCUSSION AND CONCLUSIONS

The results in Table I appear to indicate that linseed oil, hence, the unsaturated triglycerides present in it, react by radical addition through the carbon-carbon double bond with themselves, with the double bond in β -methylstyrene, and even with the aromatic nuclei of guaiacol. Cross-linking of linseed oil with itself appears, from the values of the rate constants presented, to be faster than the reaction with the carbon-carbon double bond in β -methylstyrene. The reaction with guaiacol appears to occur, but it is, however, erratic and only two reliable values of the apparent rate constant were obtained. These are of a comparable degree of magnitude than those obtained in the reaction with β -methylstyrene. The bimolecular processes occurring are several, namely, autocondensation of linseed oil unsaturations, reaction of linseed oil unsaturations with β -methylstyrene unsaturations, autocondensation of β -methylstyrene, and reaction of linseed oil unsaturations with the aromatic nuclei of guaiacol.²

At 25°C with UV irradiation, the reaction of linseed oil alone appears to be of one order magnitude slower than at 50°C. The reaction with styrene appears instead to proceed at comparable rates at 50 and 25°C + UV irradiation. Furthermore, at ambient temperature (25°C), the reactions of linseed oil alone and with β -methylstyrene proceed at the same speed. Both cases, however, indicate that at ambient temperature the UV radiation will initiate both autopolymerization of the finish as well as its fixation to the wood.

Addition of a cobalt naphthenate/MEKP radical generator couple increases the rate of both reactions quite noticeably, with the reaction of linseed oil alone being two

Table I Second-Order Rate Constants in Liters \times Mol $^{-1} \times$ s $^{-1}$ of the Reactions of Linseed Oil with Itself, with β -Methylstyrene and with Guaiacol

Conditions (°C)	Alone	Linseed Oil with β -Methylstyrene	With Guaiacol
50	1.34×10^{-4}	1.67×10^{-5}	1.60×10^{-5}
70	1.35×10^{-4}	5.30×10^{-5}	—
80	2.26×10^{-4}	4.80×10^{-5}	4.20×10^{-5}
100	2.45×10^{-4}	3.00×10^{-5}	—
25 + UV	1.48×10^{-5}	1.49×10^{-5}	—
50 + Co $^{2+}$ /MEKP	3.00×10^{-2}	5.45×10^{-3}	—

orders of magnitude faster; the reaction with β -methylstyrene is also two orders of magnitude faster. However, the addition of the radical generator couple increases the rate of reaction of linseed oil with the C—C double bond of methylstyrene faster than that of linseed oil alone. This indicates that the presence of the Co naphthenate/MEKP couple, at parity of all other conditions, would increase the percentage of cross-linking between the wood and the finish and, by inference, possibly, the durability of the finish.

These findings indicate which are the likely sites of reaction between a linseed oil finish, or a linseed oil-based alkyd finish, and the wood surface. It confirms that reaction to form covalent cross-links between finish and substrate, to possibly give longer finish durability, can occur. It also gives an indication of the relative percentages of finish self-polymerization and reaction with the wood.

REFERENCES

1. M. Paauw and A. Pizzi, *J. Appl. Polym. Sci.*, **42**, 1377 (1991).
2. M. Paauw and A. Pizzi, *J. Appl. Polym. Sci.*, **43**, 1585 (1991).

A. PIZZI
D. L. WATSON

Department of Chemistry
University of the Witwatersrand
Johannesburg, South Africa

Received July 9, 1990

Accepted December 17, 1991