NEW CHEMICALS -----

DEVELOPMENT OF MICROEMULSIONS

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Abstract: This paper describes the unique properties of microemulsions and their potential as water-based formulations for water insoluble isothiazolone biocides, or other water repellent biocides for wood protection. Water dilutable microemulsions of 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one have been prepared and evaluated in wood impregnation treatment due to its excellent fungal and insect protection properties. Detailed analyses of microemulsion-treated wood has revealed good penetration of the active ingredient, compared to emulsion- and solvent-borne formulations. Leaching of the active ingredient from the treated wood was found to be a function of the surfactant systems in the microemulsions.

Key words: microemulsion, isothiazolone, water-dilutable, penetration, leachability, fungal decay, termite attack and vacuum impregnation

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INTRODUCTION

Solid wood is a complex porous matrix material possessing a large surface area in equilibrium with water [1]. The macro- and microdistribution of wood protection biocides within the matrix is extremely important for the performance of wood in different end uses. The ideal wood protection biocide should provide bioefficacy against fungal decay and termite attack, deep wood penetration and fixation of the active ingredient inside the wood. It is essential, therefore, that the biocides are properly formulated to maximize their effectiveness as wood preservatives. At present, there are three major types of formulations for wood protection biocides : 1) aqueous solutions, 2) solvent borne solutions and 3) oil-in-water emulsion formulations [2].

Many wood protection biocides possess very low water solubilities and are unsuitable for aqueous systems. Increased environmental pressures have caused the wood protection industry to move toward aqueous systems and away from solvent-based systems. The oil-in-water emulsions make possible the impact of water-repellent chemicals in aqueous situations, which provides some improvements in product quality. However, these conventional emulsions have unfavorable characteristics, such as a tendency toward phase separation upon dilution with water, undesirable large oil droplet size (more than 10^{-8} m) with broad size distribution, and high solvent content. The large droplet size and non-uniform size distribution may cause poor penetration of the active ingredient into the wood. The phase separation is not favorable to formulation storage, treatment process and safety considerations.

Microemulsions [3] are different from the conventional emulsions. They are transparent to the eye, thermodynamically stable and of low viscosity. In these microemulsions, water and hydrocarbon spontaneously form an oil-in-water "emulsion" or a water-in-oil "emulsion". These "emulsions" contain uniform and nanometer-size oil droplets in a continuous water phase, or water droplets in a continuous oil phase under certain circumstances.
The theoretical evaluation of the stability, solubilization and other properties of microemulsions have been a major focus of extensive research interests during last decade [4]. These research interests have been emphasized by the economic importance of microemulsion technology in tertiary oil recovery, cosmetics, drugs, chemical processing and biocides [5,6,7].

A microemulsion dispersion system has several major features which are considered important for its technological application in wood protection formulations. The thermodynamically stable microemulsion has no tendency toward phase separation; the tiny droplet size (10 to 100 nm) and uniform size distribution offer a high active ingredient loading in an incompatible medium. The excellent dispersion of the active ingredient provides it sufficient contact with microorganism in real application systems; The ultralow interfacial tension will influence surface wetting and penetration of the active ingredient through porous materials such as wood. Therefore, the development of the microemulsion technology could give us the opportunity to supply new wood protection biocides which have enhanced qualities such as stability, compatibility, bioefficacy and ease of use.

During the last decade wood protection research has featured an effort directed toward developing novel biocides. One of these is the substituted isothiazolone (ITA) compound, 4,5 dichloro-2-n-octyl isothiazoline-3-one, which has been identified as a broad spectrum wood protection biocide in an oil-borne formulation for wood in ground contact [8, 9]. Our recent work has been concerned with formulating this ITA compound as a water dilutable microemulsion form. In this paper we present preliminary results on wood penetration and leachability of the ITA compound from different water dilutable microemulsions. These data are compared to solvent borne formulation and emulsifiable concentrate (EC) formulation.

MATERIALS AND METHODS

Wood blocks of Southern Yellow Pine sapwood were vacuum impregnated according to American Wood-Preservers' Association (AWPA) Standard M10-77. Four different microemulsions, an EC and a toluene solvent formulation of the ITA were used to treat the wood (Table 1). The treated wood was analyzed to determine the depth of penetration and leaching of the ITA.

Table 1. ITA Concentration of Treatment Formulations

Formulation Code	Formulation Type	ITA Conc. in Formulations, wt%
A	ME	0.20
B	ME	0.25
C	ME	0.05
D	ME	0.20
EC	EC	0.20

Depth of penetration

The end grain surface of 50x100x600 mm (2"x4"x2') wood blocks were sealed and impregnated. The treated wood blocks were air dried for seven days. A 50x50x150 mm (2"x2"x6") piece was cut from the center of these blocks and then sectioned to slices to determine depth of penetration. The depth of penetration was measured at five levels for the wood blocks treated by the microemulsions and EC, while the solvent treated wood was determined at three levels. Each slice was extracted by methanol and the active ingredient was analyzed by high performance liquid chromatograghy (HPLC).

Leachability

Leaching of 1.6x19x152 mm treated wood blocks was completed by using a modification of AWPA Standard M 11-87. After air drying for seven days, the treated blocks were immersed in 100 parts of D.I. water per volume of wood. The leachate was removed at 6 hours, 1, 2, 4, 14 days and replaced with fresh D.I. water at the same time. The ITA concentration in every leachate was analyzed by HPLC.

RESULTS AND DISCUSSIONS

Detailed analyses of wood blocks treated with different ITA formulations revealed good penetration of the active ingredient into the wood. The ITA concentration determined on the wood surface, that is in the 0-1 mm layers, was designated as 100, with the active ingredient in the other layers represented as a percentage of this value. The results are summarized in Table 2. These results indicate that the retention gradient of the ITA in the wood treated with different microemulsion systems were comparable to or better than that of either the solvent borne formulation or the emulsion formulation. There was about 55 % ITA found at a depth of 14 -15 mm in the wood blocks treated by the microemulsion D in comparison to the emulsion formulation where 9.0 % of the ITA was found at the same depth in the wood. In contrast to the emulsion the microemulsion has very low water-oil interfacial energy as described before, which offers better wettability and reduced resistance for water-repellent ITA molecules to penetrate into the deeper parts of the porous wood matrix. It is not reliable to compare penetration performance between the microemulsion and the solvent formulation since there is a lack of penetration date at the 14-15 mm depth in the solvent formulation system.

Table 2. Penetration of ITA from Water Dilutable Microemulsions into 50 mm Thickness Impregnated Southern Yellow Pine

Depth (mm)	Water dilutable formulations				
	A	B	C	D	EC
0-1	100	100	100	100	100
2-3	51	50	29	56	69
4-5	45	45	23	61	64
7-8	42	46	21	61	54
14-15	25	33	11	54	9
	Solvent borne formulation				
0-3	100				
3-6	55				
6-10	38				

A general feature of the penetration behavior of the microemulsions was the presence of distinct gradients (Figure 1). The ITA retention decreased to 30 to 60 % after it penetrated through the outer surface (0 to 1 mm layer) of the wood block. This level became almost constant up to the depth of 14-15 mm. The penetration profiles were a function of different microemulsion formulations. Our results indicate that formulation components, such as surfactants and solvents, will cause different effects on the ITA penetration profile because of their characteristic interactions with wood components such as lignin and cellulose.

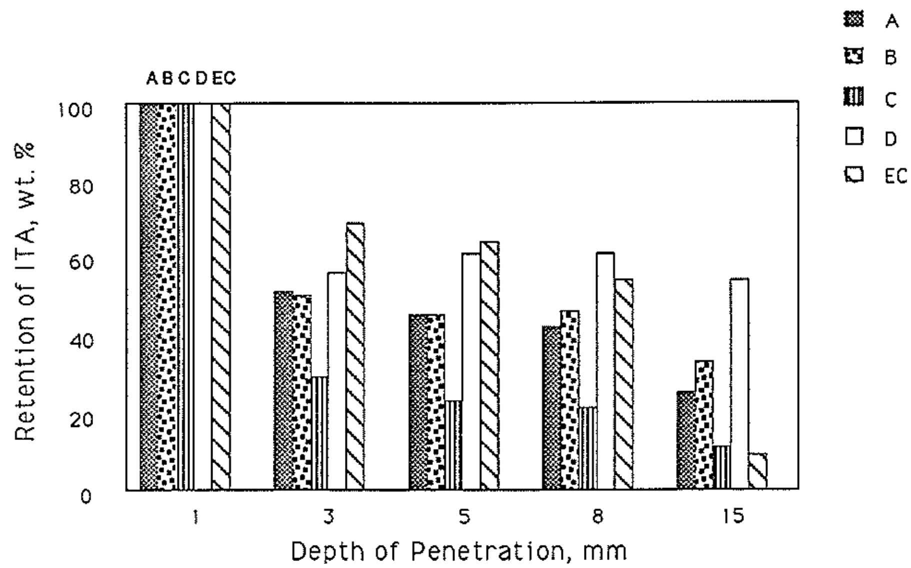

Figure 1. Wood Penetration of ITA from Water-dilutable Microemulsions

The leachability of ITA from wood was also found to be a function of formulation type. The cumulative leaching behavior of the ITA from the treated wood is shown in Figure 2. The ITA concentration in the leachate at different time intervals represents average leaching rate of the ITA from the treated wood. The wood treated with the emulsion formulation and three of the microemulsion formulations have a faster leaching of the ITA than the solvent borne formulation. We consider that the difference in the ITA leachability from different microemulsions is due to different interaction patterns between wood components and surfactants, cosurfactants and solvents in the formulations. Our future research effort will be directed toward understanding the effect of formulation additives on this variability.

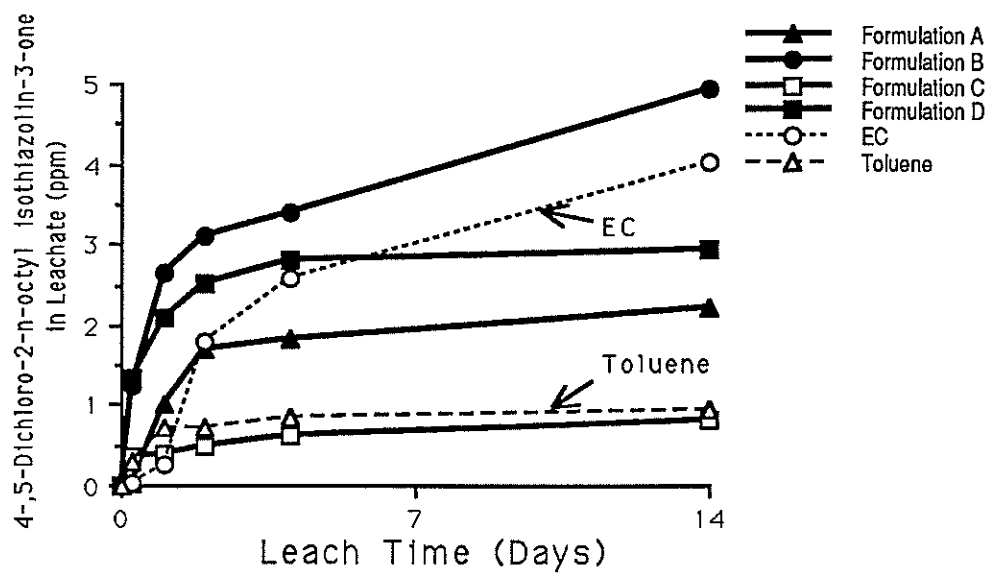

Figure 2. Cumulative Leaching of Active Ingredient from Water Dilutable Microemulsions

CONCLUSIONS

Water-dilutable microemulsions are favorable formulations in wood protection due to 1) their ability to keep the active ingredient homogeneous for long periods in the treatment process, 2) then decreased hazard accociated with decreased solvent, and 3) their compatibility in wood treatment systems. This technology is recommended for the wood protection industry. The initial results in this study provided good informationconcerning wood penetration and leachability. Further work is needed to fully understand the interaction of the microemulsion system with wood and to optimize its performance in wood protection.

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