EVALUATION OF ENCAPSULATED AND GELLED CHLOROPICRIN FORMULATIONS FOR USE IN WOOD POLES

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ABSTRACT

Gelling (increasing a fluid's viscosity) and encapsulation were evaluated as means to improve the handling properties of the fumigant chloropicrin during application in the remedial preservative treatment of poles and other timbers. Several gelling agents, at concentrations of <5% (w/w), were capable of increasing the viscosity of chloropicrin above 100,000 centipoise. The form of the dispensed gel allowed for a reduced surface area during application (when compared to liquid chloropicrin) and volatility of the gelled formulation was effectively reduced. However, addition of gelling agents to chloropicrin did not reduce the relative volatility from equivalent exposed surface areas. An evaluation of methods for dispensing one gelled formulation identified a modified pressure cylinder as a means for safer and easier application of chloropicrin compared with currently used methods. Polymer tubes for encapsulation were also evaluated as a means of handling and dispensing both liquid and gelled chloropicrin.

Keywords: Chloropicrin, fumigant, wood, poles, gel, encapsulate, preservative.

Fumigants have been used commercially for the last sixteen years to control decay in utility poles and other wood products (Graham and Corden 1982; Goodell et al. 1980). Although effective, fumigants can be difficult and potentially hazardous to use. One fumigant registered for use in poles, chloropicrin (a type of tear gas), is a powerful lachrymentor and thus is particularly difficult to use. Conventional application methods require that holes be bored into a pole or other wood product and the fumigant poured as a liquid into these holes (Graham and Helsing 1979). Because poles and other timbers often contain checks and other defects liquid chloropicrin often escapes from the pole in the treatment process with potential hazard to the applicator.

As part of our research to develop improved methods for the application of wood preservatives to the groundline region of utility poles,[1] we have been investigating methods to improve the effectiveness and ease of delivery of fumigants in remedial treatments. To improve its handling properties, we explored the possibility of gelling and of encapsulating chloropicrin. Gelling has been attempted previously to improve the properties of soil applied fumigants (White 1983). However, gelled fumigants are no longer being produced or marketed for this purpose and they have not yet been tested in wood. Encapsulation has also been used to allow easier handling of fumigants and some work has been initiated with

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TABLE 1. *Performance of chloropicrin/gel formulations.*

Gelling agent (manufacturer)	Performance comments[1]	
1. Alumagel (Witco)	+++	liquification over time
2. Aluminum Octoate (Witco)	+	10% required to gel[2]
3. Sodium Stearate (Witco)	+	gelling agent separates from chloropicrin over time
4. Imbiber Beads #1309 with wicking element (Enco)	++	>5% required to gel
5. Imbiber Beads #1309 (Enco)	++	>5% required to gel
6. Imbiber Beads B 1318S (Enco)	+++	
7. Cab-O-Sil (Cabot)	+++	
8. Methocel F4M-PRG (Dow Chemical Co.)	++	requires methanol as co-solvent
9. Methocel J75MS (Dow Chemical Co.)	++	requires methanol as co-solvent
10. Methocel HB (Dow Chemical Co.)	++	requires methanol as co-solvent
11. Klucel H (Hercules)	+++	
12. Klucel M (Hercules)	++	>5% required to gel
13. Klucel CMC (Hercules)	+	no gelling, 15% required for gelling
14. Water Lock (Grain Processing)	+	no gelling, 15% required for gelling
15. Sta-Wet (Polysorb)	+	no gelling, 15% required for gelling

[1] A performance rating of +++ indicates that a gel could be formulated with 5% (w/w) gelling agent or less, without the need of a co-solvent. The rating system is a relative means of comparison provided for reader convenience and the comments indicate why a formulation was downrated.

[2] Amount of gelling agent (w/w) required to gel chloropicrin with a viscosity of 100,000 CP or greater.

regard to encapsulated fumigant use in wood (Cooper 1974; Zahora 1983). Cooper (1974) has previously reported on a laboratory evaluation of polyethylene vials for the slow release of fumigants in wood.

Both gelling and encapsulation provide for a means of reducing the volatility and leakage of fumigants during handling. In our study we looked at several different methods of performing both procedures. After selection of appropriate methods, we looked at techniques to apply the reformulated chloropicrin to wood in a manner that would be simpler and more rapid than currently used methods and that would be safer and easier for an applicator to use.

PROCEDURES

Gel formulation, selection, and application

Fifteen commercially available gelling agents including metallic-based soaps, adsorbent beads, silica materials, and modified cellulose, were explored for use in improving the handling properties of chloropicrin (Table 1). The performance standards that we set for an appropriate gelling agent were that the gel should:

1) be formed with a minimum volume of gelling agent to obtain gelled viscosity of approximately 130,000 centipoise,
2) show no decrease in viscosity with time,
3) have appropriate thixotropic properties allowing it to flow under mild pressure,
4) reduce the effective volatility of chloropicrin during application,
5) allow release of virtually all of the chloropicrin from the gel matrix after application, and
6) be cost-effective.

TABLE 2. *Concentration of chloropicrin in the headspace above gelled formulations.*

Gel	Average ppm	Standard deviation ppm
Cab-O-Sil	34,345	4,899
Klucel H	17,999	2,782
Imbiber Beads	18,543	2,511
Alumagel	22,708	4,113
Control	16,506	2,422

The gels were formulated at concentrations of 0.5 to 15% (w/w) gelling agent. Materials that did not sufficiently gel chloropicrin at concentrations of 15% were dropped from this study after initial testing. The addition of over 15% inert ingredient would severely limit the amount of active ingredient (fumigant) that could be applied to a timber. Viscosity of the gels was tested using a Brookfield spindle-type viscometer.[2] The target viscosity of 130,000 centipoise provided for a gelled material that would flow under mild pressure but would not leak from checks or cracks in the wood under the influence of gravity alone.

A relative estimate of the volatility of the chloropicrin was obtained by gas chromatographic (GC) analysis of the vapors released from gels or from non-gelled chloropicrin. Both gels and liquid chloropicrin were placed in containers that provided a uniform exposed surface area of 40.7 cm^2. The method of analysis used to determine the concentration of chloropicrin vapors liberated from the gel surface was as follows: A gas-tight syringe was fitted to a rigid polyethelene cover, which served as an air-tight seal on a container holding the liquid or gelled chloropicrin. The cover was placed over the gel for 5 minutes, after which a one cm^3 gas sample was drawn into the syringe and injected into a gas sampling valve for GC analysis. Four samples were withdrawn from each formulation and average values obtained.

GC analysis was performed on a 5M fused-silica, macro-capillary column with a methyl silicone liquid phase. The column temperature was 35 C, and detection was by flame ionization.

Evaporative tests of the gels were also performed to compare with the GC analysis and to determine how much chloropicrin residue was retained by each matrix after evaporation at ambient conditions.

Following the selection of an appropriate gelling system, a means of delivering the gelled fumigant to poles and timber in the field was explored. The criteria for this delivery system were that application be safe, easier to use than current systems, and would provide a similarly effective treatment when compared to current remedial treatments with fumigants.

Encapsulation

Several commercial polymers formulated into tubes were tested for their ability to contain chloropicrin over long periods of time at ambient and at an elevated temperature (65 C). Six polymer tubes were selected for testing after initial screening, excluding those that ruptured or dissolved (polysulfone, polycarbonate) within

[2] Brookfield Engineering Laboratories, Inc., 240 Cushing Street, Stoughton, MA.

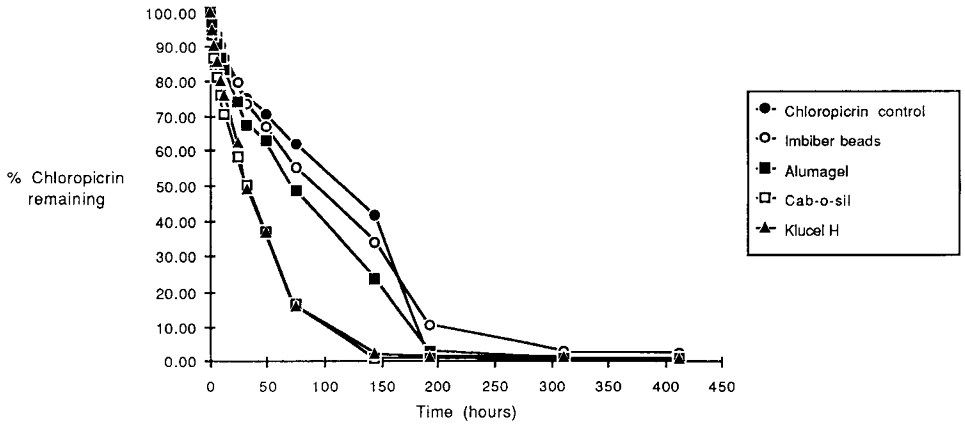

FIG. 1. Evaporative loss of chloropicrin from four gels. These data are from tests of individual gel formulations, however, two other evaporative loss studies (data not presented) were performed and provided similar results.

24 hours of the application of chloropicrin either at ambient or elevated temperatures. [See the Results and Discussion section for a listing of these polymeric tubes.] Rubber stoppers were used to seal the open ends of the tubes and the surface area of each tube was calculated. Glass tubes sealed with rubber stoppers were used as controls. Diffusion of the fumigant through the polymer walls and subsequent evaporative loss were evaluated by weighing the tubes periodically. A visual inspection of the tubes for evidence of deterioration was also made. The values in Table 4 are averages from two tubes of each polymer tested.

RESULTS AND DISCUSSION

Gelling

Table 1 presents a comparison of the gelling-agent/chloropicrin formulations based on the amount of gelling agent volume required and if a co-solvent was required to produce a gel of greater than 100,000 cp. Formulations were downrated if greater than 5% (w/w) gelling agent was required to obtain a viscosity of 100,000 cp. Based on these parameters, four formulations were identified as the most promising upon which to conduct further analysis with regard to volatility and cost.

TABLE 3. *Cost analysis of gelling agents based on a target viscosity.*

Gelling agent (manufacturer)	Concentration of gelling agent based on a target viscosity	Cost/# of gelling agent ($)	Cost/pint of gelled chloropicrin ($)
Cab-O-Sil (Cabot)	4.0%	2.96*	0.20
Alumagel (Witco)	4.5%	2.16**	0.17
Klucel H (Hercules)	4.0%	4.50***	0.31
Imbiber Beads (Enco)	4.0%	4.90****	0.33

* Lot size = 560–1,950 lbs.
** Lot size = less than 2,000 lbs.
*** Lot size = 200–1,900 lbs.
**** Lot size = less than 1,000 lbs.; if 1,000–2,000 lbs. purchased, then cost per pint = $0.29.

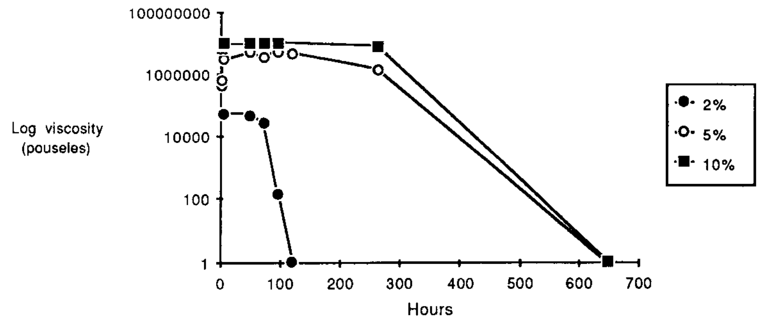

FIG. 2. Loss in viscosity of 2%, 5%, and 10% alumagel/chloropicrin gels over time.

The GC volatility data for these four are presented in Table 2. The release rates of chloropicrin from the gel matrix and chloropicrin residue remaining in the gel are presented in Fig. 1. None of the gels reduced the volatility of chloropicrin and some appeared to increase its volatility and rate of evaporative loss. The chloropicrin residue remaining in each formulation after evaporation for 400 hours at ambient temperatures was less than 2% w/w. These four agents were also compared for cost (1986 cost figures, Table 3).

Alumagel (Witco Corp.) was one of the most effective agents in gelling chloropicrin and it was also the most cost-effective agent. However, because the viscosity of alumagel/chloropicrin formulations decreased over time (Fig. 2), Cab-O-Sil (a fumed silica) was selected as the most appropriate agent for further testing. The alumagel-chloropicrin formulation was the only gel that exhibited this loss of viscosity over time.

Several means of delivering the gelled chloropicrin to timbers were evaluated in addition to the use of polymer tubes (discussed below). Polyethylene caulking tubes were effective for the delivery of chloropicrin gels, but the delivery rate into the pole and the volume that could be delivered from one caulking tube was too low for efficient use. Grease pumps and continuous feed caulking guns were studied for use but were rejected after initial tests because of the difficulties in sealing the applicators and in transferring the pumping apparatus from one gel supply to another.

The most effective application method tested was the use of a pressurized cylinder provided by the basic manufacturer of chloropicrin,[3] that was modified to accept a high pressure hose fitted with a metal tube for delivery of the gel into holes bored in poles and timbers (Fig. 3). The addition of a stem valve to the cylinder also provided for a system that could be pressurized in the field through use of a hand pump.

Although the volatility of chloropicrin was not reduced after formulation with Cab-O-Sil, gelling did alter the dispensed form of the chloropicrin so that when applied to a pole, a reduced surface area was exposed to the atmosphere (Fig. 4). [The gel is extruded providing for more limited surface area than a similarly dispersed conventional liquid formulation.] Laborers performing experimental

[3] Great Lakes Chemical Co.

FIG. 3. Application of gelled chloropicrin into pole with a pressurized tank system.

work with chloropicrin reported that they could apply the gelled formulation with greater ease and without the use of a respirator. The reported greater ease in handling may be due to a reduction in volatilized chloropicrin due to a reduced surface area of the gel. Gelling does not eliminate the lachrymentory properties of chloropicrin however, and reasonable care must still be exercised in applying the gel.

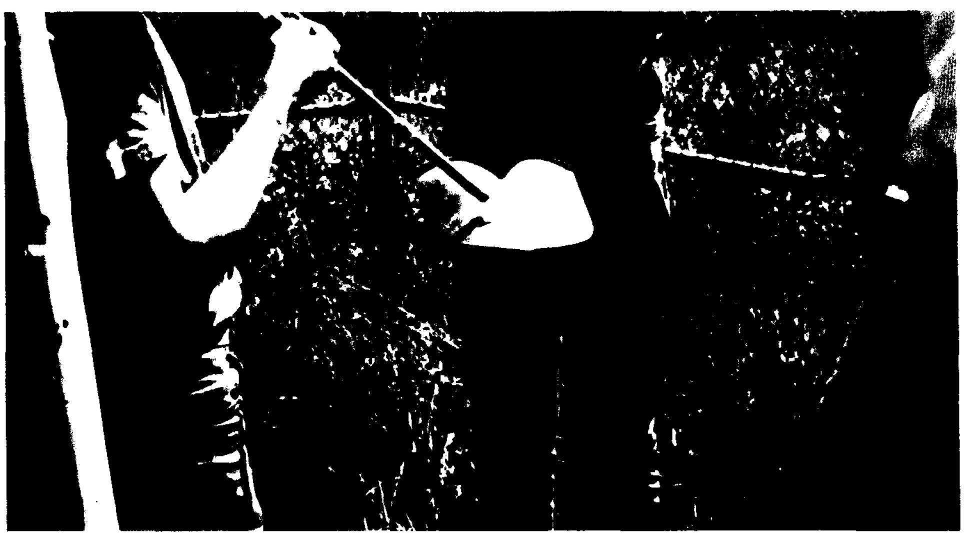

FIG. 4. Form of dispersed Cab-O-Sil chloropicrin gel.

TABLE 4. *Evaporative loss of chloropicrin from, and cost of plastic formulated into tubes for encapsulation.*

				Tube characteristics[1]			
		Average evaporative loss of CP	Cost/ tube*	L	ID	T	V
Rank	Tube (material)	(gr/wk/sq cm)	($)		mm		ml
1	Applied Plastics (polyethylene)	0.046	0.055	152	16.5	0.98	32.5
2	Applied Plastics (polypropylene)	0.049	0.055	152	16.5	0.98	32.5
3	Starstadt *55.510 (polypropylene)	0.067	0.078	130	14.3	1.2	17.5
4	Starstadt #60.554 (polypropylene)	0.103	0.074	118	15.0	1.2	15.0
5	Starstadt #97.65.90217 (block copolymer of polypropylene and polyethylene	0.195	1.333	111	14.5	0.5	18.0
6	Osmose (undisclosed polymer)	0.227	NA	228	15.5	—	43.0
7	Glass tube (control)	0.001	NA	130	14.3	1.7	—

NA = not available.
* All tube costs were based on prices for lots of 50,000.
[1] L = length, ID = inside diameter, T = thickness, V = volume.

Polymer tube encapsulation

The rate of evaporative loss of chloropicrin from the tubes relative to their surface area was constant over a 35-day period. These rates are shown in Table 4. The rubber stoppered glass test tube samples released negligible amounts over the test period; thus, release from the polymer tubes can be attributed to diffusion of chloropicrin through the walls of the tubes. Although it was not the intent of this study to explore the use of the tested polymers for the controlled release of fumigants in poles, all of the polymers analyzed functioned in this manner and none were completely impermeable to chloropicrin. The most durable polymer was a black linear-polyethylene tube.[4] The tube from Osmose Co.[5] was the most permeable tube tested. However, it should be noted that this later tube is designed to break down and rupture after exposures of 6 to 72 hours to chloropicrin (Fahlstrom 1982).

An analysis of the diffusion and loss of chloropicrin in gelled formulation through the polymers was not performed in this study. However, both gelled and liquid chloropicrin have been applied to test timbers in this encapsulated form. The tubes can be inserted into the downward sloping holes that are bored in poles for use in conventional remedial pole treatment with fumigants. Gelling of chloropicrin prior to encapsulation in a tube eliminates the hazard of the liquid fumigant leaking from the hole through checks in the pole after rupture release of the chemical from the tube.

CONCLUSIONS

The viscosity and evaporative loss of the fumigant chloropicrin can be reduced during application through the use of commercially available gelling agents. Both gelled and liquid chloropicrin can be contained in polymer tubes that can be inserted into poles through holes bored for conventional treatment with fumigants.

[4] Applied Plastics Co.

[5] Osmose Company, Buffalo, NY.

Although all polymers tested were permeable to chloropicrin, polyethylene was the least permeable. All polymers tested, however, would provide for the controlled release of chloropicrin into a pole if this was desired.

A pressurized cylinder, modified to dispense gelled chloropicrin, allowed for pole treatment and fumigant application in a manner that is safer and easier than conventional application methods.

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