A mining research contract report
May 1982

FURTHER STUDIES ON OPTIMUM COMBINED FIRE RETARDANT / PRESERVATIVE TREATMENTS AND STENCH WARNING SYSTEMS FOR WOOD MINE TIMBER

Contract JO 166068
Springborn Laboratories, Inc.
Enfield, Connecticut 06082

OFR
83-27

BUREAU OF MINES ★ UNITED STATES DEPARTMENT OF THE INTERIOR
Mining Research

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REPORT DOCUMENTATION PAGE

1. Report No.	2.	3. Recipient's Accession No.

4. Title and Subtitle
Further Studies on Optimum Combined Fire Retardant/ Preservative Treatments and Stench Warning Systems for Wood Mine Timber

5. Report Date
May 1982

6.

7. Author(s)
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8. Performing Organization Report No.
6073.1

9. Performing Organization Name and Address
Springborn Laboratories, Inc.
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Enfield, CT 06082

10. Project/Task/Work Unit No.

11. Contract or Grant No.
JO 166068

12. Sponsoring Organization Name and Address
U. S. Department of the Interior
Bureau of Mines
Washington, D.C. 20241

13. Type of Report
Final (Apr. 1981 - May 1982)

14.

15. Supplementary Notes
Previous reports covering work conducted under this contract include: "Combined Fire/Rot Retardant Treatment for Wood Mine Timber", October 1978, NTIS PB81-166381, "Research on Combined Fire/Rot Retardant Treatment for Wood Mine Timber", September 1979, NTIS PB81-244493

16. Abstract

As a follow-on to previous investigations, reduced treatment levels for the optimum fire retardant/preservative system were evaluated. An impregnation of 3.5 lbs/ft^3 of Fyreprufe followed by 3.5 mils of Albi 107A plus an Albi 144 top coat provides adequate flammability and flame spread protection. However, there is a significant loss in compressive strength at this retention level, particularly parallel to the grain.

A pilot-size pressure impregnation cell was installed for use in treating larger quantities of wood.

Based on the optimum fire retardant/preservative treatment system - Fyreprufe/ACC impregnation followed by Albi 107A/144 intumescent paint - a model treatment process was developed, capable of handling 3 million board feet per year. Associated annualized costs per thousand board feet (K bd. ft.) for treating 12" x 12" timber were calculated to be:

Impregnation:	$ 63.00/K bd. ft.
Coating:	$112.00/K bd. ft.

A literature search was conducted to identify materials and techniques suitable for a localized stench warning system for heated mine timbers. Based on this review, a number of stench warning concepts were developed. Those based on surface coating were given a preliminary laboratory evaluation.

17. Originator's Key Words
Flammability
Mine Timber
Preservatives
Fire Retardants
Stench Agents
Mercaptans
Intumescent Paint

18. Availability Statement
Availability Unlimited

19. U. S. Security Classif. of the Report	20. U. S. Security Classif. of This Page	21. No. of Pages	22. Price
Unclassified	Unclassified	80	

FOREWORD

This report was prepared by Springborn Laboratories, Inc., Enfield, Connecticut under USBM Contract number JO 166068. The contract was initiated under the Metal and Nonmetal Mine Health and Safety Program. It was administered under the technical direction of Pittsburgh Research Center with Dr. Charles Lazzara acting as Technical project Officer. Mr. J. Connelly was the contract administrator for the Bureau of Mines. This report is a summary of the work recently completed as part of this contract during the period April 1981 to May 1982. This report was submitted by the authors on May 12, 1982.

TABLE OF CONTENTS

Table of Contents - (Continued - 2)

LIST OF FIGURES

LIST OF TABLES

SUMMARY

As a follow-on to previous investigations[1,2], Fyreprufe was investigated at reduced treatment levels in Ponderosa pine test samples. Pine was impregnated with both 3.5 and 4.5 pounds/ft^3 of Fyreprufe plus 1.0 pounds/ft^3 of acid copper chromate. Samples with both treatment levels were coated with both 3.5 and 7.0 mils of Albi 107A intumescent paint plus a 1 mil top coat of Albi 144.

Treated material was tested for flame spread by two foot tunnel; flammability per ASTM E-69-80, "Combustible Properties of Treated Wood by the Fire Tube Apparatus"; and compressive strength per ASTM D-143. An impregnation of 3.5 pounds/ft^3 of Fyreprufe followed by 3.5 mils of Albi 107A plus an Albi 144 top coat provided a flame spread rating of 26.7 and a weight loss in the fire tube of 10.7%.

There was a substantial loss in compressive strength for the impregnated pine, particularly in the direction parallel to the grain. Losses ranged from 30 to 50%.

A pilot size pressure impregnation cell was installed and plumbed for use in treating larger quantities of wood by the full cell method.

Based on the optimum fire retardant/preservative treatment system - Fyreprufe/ACC impregnation followed by Albi 107A/144 intumescent paint - a model treatment process was developed, capable of handling three million board feet per year. Associated annualized costs per thousand board feet (K bd. ft.) for treating 12" x 12" timber were calculated to be:

Impregnation: $ 63.00/K bd. ft.

Coating: $112.00/K bd. ft.

These manufacturing costs compare favorably with the current price for cut and framed 12" x 12" timber of approximately $400 to $600 per K bd. ft.

A literature search was conducted to identify materials and techniques suitable for a localized stench warning system for heated mine timbers. Based on this review, a number of stench warning concepts were developed, including polysulfide coatings, polymer/stench agent salt based coatings, oil soluble polymeric fixative coatings, and coatings based on odorants chemically bonded to a polymer.

A number of candidate coatings were given preliminary laboratory evaluation.

1. INTRODUCTION

Wood structures constitute the major shaft and roof support in underground noncoal mines. There are, however, two distinct problems with extensive use of wood in underground mines. First, as a combustible material, mine timber constitutes the major fuel loading and hence increases the potential for a large fire in the mine. Second, as a natural cellulosic material, mine timber is subject to fungicidal attack with destruction of its structural properties, and hence requires continual replacement and care in order to maintain safe supports. Rotted mine timber is often more flammable than sound timber, so that rotting could also contribute to the fire hazards in a mine.

The average life of untreated wood in underground mines is about three years, but with suitable fungicidal treatments such as chromated zinc chloride or fluor chrome arsenate phenol, the lifetime can be extended to 10-20 years. However, such wood treatments do little for improving fire retardancy and in some cases actually increase the fire hazards by increasing the wood flammability and toxicity of the combustion products. On the other hand, common fire-retardant treatments for wood, such as ammonium phosphates and sulfate, may not be compatible with decay resistance. Also, there is some question as to whether or not such common fire retardants are effective in underground mine fire situations.

During initial studies (June 1976 to October 1978) combined preservative/fire retardant systems were pressure impregnated into Douglas Fir and Ponderosa pine samples and evaluated for decay, flammability, and mechanical properties.[1]

First, thirty systems, based on combinations of commercially available preservatives and fire retardant impregnants and coatings, were applied to Douglas fir samples and evaluated for decay and flammability. The ten most promising systems were applied to both fir and pine and reevaluated for decay and flammability before and after water leaching.

The five best systems were given a thorough laboratory evaluation using both pine and fir. Evaluations included flame spread, smoke density, toxic gases, decay, compressive strength, flammability after artificial weathering, and cost.

All systems had acceptable toxic gas levels and smoke densities, but flame spread was only borderline acceptable for most of the samples tested. A trade-off analysis showed Fyreprufe/Acid Copper Chromate impregnation with Albi 107A/144 intumescent paint and Koppers NCX impregnation to be the best systems.

Additional work between October 1978 and October 1980 focused on more novel approaches.[2]

These additional systems can be categorized as follows:

- Systems using a highly hydrated salt impregnant as the fire retardant (bound water)
- Systems with a polyester coating containing a highly hydrated mineral filler as the fire retardant (bound water)
- Systems using built-in reservoirs of treatment chemicals for "time release"
- Systems based on salt impregnation plus controlled post-charring of the surface for reduced flame spread
- Fyreprufe/Acid Copper Chromate (ACC) at a high level of retention and other miscellaneous systems.

To conduct a screening evaluation of these concepts, wood samples were impregnated, coated and evaluated for flammability per ASTM E-69-80, Procedure B, "Combustible Properties of Treated Wood by the Fire Tube Apparatus", both before and after water leaching. A total of thirteen systems were tested. Leaching was done by total immersion of the samples for a period of four days.

The most promising four systems from the initial evaluation were then given more thorough testing for decay resistance by Soil Block Method (ASTM D-1413), smoke density and toxic gas analysis (NBS procedure), flame spread by two foot tunnel, and compressive strength both parallel and perpendicular to the grain (ASTM D-143).

To facilitate handling and impregnation, Ponderosa pine was used for all the evaluations. This is a highly porous wood which permits full penetration during pressure impregnation. As was done in our initial investigations, all test samples were precut to size prior to treatment; all impregnation was by the full cell method.

The culmination of this additional effort was a trade-off analysis and recommendation of the best treatment system for larger scale evaluation. The most promising system on the basis of history of usage in the mine, ease of application, and low cost as well as overall performance was the Fyreprufe/ACC impregnation with Albi 107A/144 intumescent paint top coating.

This report describes final investigations conducted under Contract JO166068 between April 1981 and May 1982 which entailed:

- Determining the effect of reduced retention and coating weight for the optimum treatment system (Fyreprufe/ACC with Albi 107A/144) on flame spread and weight loss in the ASTM E-69 fire tube,
- Developing a model manufacturing process for timber treatment and associated annualized costs per thousand board feet,

- Installing a pilot-size pressure impregnation cell suitable for treating large quantities of wood for evaluation by the Bureau of Mines Pittsburgh Research Center in simulated mine tunnel fires,

- Conducting a literature search on stench warning materials and techniques,

- Developing possible stench warning concepts using materials which can be included in the fire retardant/preservative treatment system,

- Conducting a preliminary evaluation of wood treated with stench warning materials.

A detailed technical discussion appears on the following pages.

2. THE EFFECT OF REDUCED RETENTION AND COATING WEIGHT ON FLAMMABILITY PERFORMANCE FOR THE FYREPRUFE/ACC BASED TREATMENT SYSTEM

Low levels of Fyreprufe/ACC impregnation treatment while fairly effective as a fire retardant, provide timber which is somewhat deficient in flame spread performance. For example, the Fyreprufe/ACC (2 and 1 pounds/ft^3)-Albi 107A/144 paint system when applied to pine yielded a flame spread rating of approximately 42 by the two foot tunnel test. When the retention of the Fyreprufe was increased to 6 pounds/ft^3, the flame spread rating dropped to 24. At the same time, however, there was a 40% loss in compressive strength of the treated wood. Therefore, during the current effort, we investigated intermediate levels of Fyreprufe (i.e., 3.5 and 4.5 pounds/ft^3) which would hopefully provide improved flame spread performance over the previous rating of 42, but which might not have such an adverse effect on compressive strength.

In addition, as a potential cost saving, we examined reduced coating thickness for the intumescent paint system.

A sufficient number of samples was precut from Ponderosa pine in order to conduct both the ASTM E-69 Fire Tube test as well as flame spread by the two foot tunnel test. The samples were marked, vacuum dried for approximately 18 hours at 60°C and preweighed prior to impregnation.

As before, the pine samples were pressure treated from an aqueous solution containing both Fyreprufe and acid copper chromate (ACC). The composition of these salts is as follows:

FYREPRUFE

Salts	Percent by Weight
ammonium sulfate	89
diammonium phosphate	5
sodium fluoride	4
sodium chromate	2

ACID COPPER CHROMATE

Salts	Percent by Weight
copper sulfate	50
sodium dichromate	48.3
chromium trioxide	1.7

The solution concentrations used for the desired retentions were as follows:

Salt Mixture	Desired Retention in the pine (lbs/ft^3)	Concentration in the Treatment Solution; % by Weight
Fyreprufe	4.5	9.25
ACC	1.0	1.90
Fyreprufe	3.5	7.20
ACC	1.0	1.90

The solutions were prepared by first dissolving the Fyreprufe in approximately 3/4 of the required deionized water. The pH was then adjusted to 3.5 with concentrated sulfuric acid. Finally, the ACC was added and the solution adjusted to the proper total weight with more deionized water.

The flame spread pieces measured 0.5 x 3.75 x 23.75 inches; to facilitate drying and treating, each board was cut in two and was later staped together again prior to painting. The fire tube pieces measuring 3/8 x 3/4 x 13 3/8 inches were also stapled together after treatment in order to produce 40 inch test specimens.

As before, impregnation was done in a 6-inch diameter by 36 inch long pressure cell. The treatment process comprised:

- Holding the samples under full vacuum (at least 23 inches of Hg), for a minimum of 30 minutes,
- Allowing the vacuum to draw treatment solution into the cell,
- Pressurizing the pieces for one hour at 150 psig,
- Using the pressure to drive residual solution out of the cell, and then
- Reweighing the wet pieces in order to determine the salt retention.

Once impregnated, the pieces were air dried in the draft of a fume hood followed by overnight drying in a $60^{o}C$ circulating air oven.

In order to investigate the effect of reduced coating weight, each set of samples was separated into two groups. One group received the intumescent base coat, Albi 107A, at the recommended coverage of approximately 7 mils of dry coating. The other group from each set received approximately half the recommended coating weight of 3 to 4 mils dry thickness. The standard 1 mil coating of the top-coat material, Albi 144, was used for all samples.

The painted samples were conditioned at $22^{o}C$ and 50% R. H. for at least two weeks prior to evaluation for flame spread by two foot tunnel and by the Fire Tube apparatus per ASTM E-69-80, Procedure B. In both cases, five samples per treatment were evaluated.

The flame spread results are presented in Table 1. From the spread ratings and the average deviations, it can be seen that there is little or no significant difference in the flame spread performance between the various treatment levels, and that 3.5 pounds/ft^3 of Fyreprufe with a 3.5 mil thick coating of Albi 107A (system A-14167) will provide acceptable flame spread protection.

Flame spread testing was also completed on control samples with and without ACC impregnation and coated with intumescent paint. For comparison, previously reported data on Fyreprufe impregnated pine have also been included (A-9834).

Flame spread for the Albi 107A/144 painted material (A-14173 and A-14174) is somewhat poorer than for the same paint applied over pine which has been impregnated with Fyreprufe (i.e., 33 versus 27 to 28 respectively). Impregnation with 1 pound/ft^3 of ACC (A-14174) has no measurable effect on the flame spread of the Albi painted samples.

Flame spread of the Firehold 10/Albi 144 painted pine samples was significantly poorer.

The fire tube test results are presented in Table 2. All four treatment levels for the Fyreprufe/ACC, Albi 107A/144 system resulted in very low weight losses in the fire tube, all less than 11%. Sample A-14162 with the heaviest treatment level was somewhat lower in weight loss than the other three samples, but the difference in flame retardancy probably does not warrant the use of the additional treatment material. Sample A-14169 with 3.5 pounds/ft^3 Fyreprufe and 3.5 mils of Albi 107A intumescent paint gave very acceptable performance with only 10.7% weight loss.

It should also be noted that the fire tube performance for the Fyreprufe/intumescent paint treated pine is superior to that for samples treated with either the Fyreprufe impregnant or the Albi 107A/144 alone. Sample A-8187 with 6.0 pounds/ft^3 Fyreprufe and no top coat lost 25.3 percent of its weight in the fire tube, while sample A-8189 with Albi 107A/144 over unimpregnated wood lost 16.8% weight on burning.

Samples were also prepared to determine the effect of 3.5 pounds/ft^3 Fyreprufe on compressive strength of the treated Ponderosa pine, per ASTM D-143. Five samples each were impregnated for testing both parallel and perpendicular to the grain, and were coated with Albi 107A/144 intumescent paint.

Compressive strength testing was conducted per ASTM D-143-52 on pine samples impregnated with both 3.5 and 3.9 pounds/ft^3 Fyreprufe; the results appear in Table 3. For purposes of comparison, we have also included previously reported data for 1.2 and 6.0 pounds/ft^3 retention levels again in Ponderosa pine. There is a wide variation in the results on different sets of control samples which can only be attributed to variations in the wood between different lots.

TABLE 1

FLAME SPREAD PER TWO-FOOT TUNNEL
ON TREATED PONDEROSA PINE SAMPLES

Sample Number	Treatment Levels		Flame Spread (1)		
	Retention (lbs/ft^3) of Fyreprufe/ACC	Thickness of Albi 107A/144 Mils	Inches	Rating (2)	Rating Average Deviation
A-14164	4.5/1.0	7/1	11.6	30.7	± 1.1
A-14165	4.5/1.0	3.5/1	11.1	27.3	± 4.8
A-14166	3.5/1.0	7/1	11.2	28.0	± 4.3
A-14167	3.5/1.0	3.5/1	11.0	26.7	± 2.7
A-9834	5.6/0.9	7.0/1	---	23.9	± 2.8
A-14174 (Control)	0/1.0	7.0/1	---	33.3	± 5.6
A-14173 (Control)	---	7.0/1	---	33.3	± 1.9
A-14172 (Control)	---	(Firehold 10/144) 7.0/1	---	65.8	± 4.6
Control	None - (untreated pine)	None	---	96.8	---

(1) Average values based on five determinations per set.

(2) Rating = $\frac{(100)}{(FS_{\text{red oak}} - FS_{\text{asbestos board}})} \times (FS_{\%} - FS_{\text{asbestos board}})$ where FS - flame spread in inches

TABLE 2

FIRE TUBE FLAMMABILITY TEST DATA (ASTM E-69-80)
FOR
FYREPRUFE/ACC - ALBI 107A/144 TREATED PONDEROSA PINE

Sample Number	Treatment System		Average Weight Loss g	% Weight Loss	Average Deviation (%)
	Fyreprufe/ACC Retention (lbs/ft^3)	Albi 107A Thickness mils			
A-8185 (Control)	None	None	61.1	83.3	± 1.2%
A-8189 (Control)	None	7.0	15.2	16.8	± 0.5%
A-9285	6/1	7.0	13.0	9.9	± 0.2%
A-14162	4.5/1	7.0	9.1	7.5	± 0.5%
A-14163	4.5/1	3.5	11.6	10.5	± 0.4%
A-14168	3.5/1	7.0	10.1	9.3	± 0.8%
A-14169	3.5/1	3.5	11.2	10.7	± 0.6%
A-8187 (Control)	6/1	None	23.7	25.3	± 0.6%

TABLE 3

COMPRESSIVE STRENGTH[1] OF FYREPRUFE
IMPREGNATED PONDEROSA PINE

Sample Designation	Fyreprufe Retention lbs/ft^3	Compressive Strength (psi)			
		Parallel to the Grain		Perpendicular to the Grain	
		Strength	% of Control	Strength	% of Control
A-7395	Control	5290 ± 630	---	1000 ± 194	---
A-7372	1.2	6720 ± 486	127	1070 ± 104	107
A-9834	6.0	4410 ± 150	55	784 ± 107	61
A-9835	6.0	4510 ± 790	56	1060 ± 163	82
A-9845	Control	7990 ± 49	---	1290 ± 188	---
A-14776:16-20	Control	5394 ± 123	---	1051 ± 103	---
A-14776: 6-10	3.9	3825 ± 173	71	921 ± 35	88
A-14177: 1- 5	3.5	2746 ± 31	51	---	---

(1) Per ASTM D-143-52

While there is an inexplicable difference between the strength values parallel to the grain for the 3.5 and 3.9 pound/ft^3 retention levels, it can generally be concluded that Fyreprufe impregnation has a significantly adverse effect on the compressive strength parallel to the grain of Ponderosa pine, at these retention levels.

It should also be noted that the strength loss perpendicular to the grain is generally less pronounced that that parallel to the grain. Since timber is much weaker in the perpendicular direction by a factor of approximately five, we would expect that timber collapse in a "cap and post" support structure would occur first in the horizontal cap. Therefore, Fyreprufe impregnation may not have all that significant an effect on the overall load bearing properties of the timber.

Also, in the case of more impermeable timber such as Douglas fir, where the depth of penetration of the impregnant is only 1/4 to 1/2 inch at best, the bulk of the timber should be unaffected.

Exterior Firex Treatment

At the recommendation of Robert Fortunato, U. S. Army Armament Research and Development Command (ARRADCOM), we evaluated Exterior Firex and Firex 352 in the fire tube (ASTM E-69). Both of these treatment systems were investigated by ARRADCOM for use with Douglas fir ammo boxes, and were found to perform very well in both the crib test (Combustible Properties of Treated Wood by the Crib Test: ASTM E-160) and in the end product for both impact and flammability.

Both impregnation systems, manufactured by Hoover-Universal, Inc., are believed to be Urea-Formaldehyde/Phosphate types. According to the supplier, treated wood has withstood accelerated weathering per ASTM D-2898, equivalent to ten years out of doors with no significant effect on flammability performance.

Southern pine fire tube samples were obtained from Hoover-Universal with both exterior Firex and Firex 352 treatments. The nominal gauge retention was 5 pounds/ft^3.

The samples were conditioned at 22°C and 50% R.H. for one week prior to testing per ASTM E-69. The results appear in Table 4. Both treatments gave very good performance with only 12.3 and 13.9% weight losses for the Exterior Firex and Firex 352 respectively.

Both materials should be considered for any future investigations.

TABLE 4

FIRE TUBE FLAMMABILITY TEST DATA (ASTM E-69-80)
FOR
EXTERIOR FIREX AND FIREX 352 TREATED SOUTHERN PINE

Sample Numbers	Treatment[1]	Average Initial Wgt.	Average Wgt. Loss	Average Percent Loss	Average Deviation
A-14199-7 to -10	Exterior Firex	158.1	19.5	12.3	± 0.4
A-14199-1 to - 4	Firex 352	139.1	19.2	13.9	± 1.2
A-8185 (Control)[2]	None	73.3	61.1	83.3	
A-14169 (Control)[2]	Fyreprufe/ACC:[3] Albi 107A/144	104.7	11.2	10.7	± 0.6

(1) Nominal 5 lbs/ft^3

(2) Ponderosa Pine

(3) 3.5 lbs/ft^3 Fyreprufe; 3.5 mils of Albi 107A

3: DEVELOP A MODEL MANUFACTURING PROCESS FOR TIMBER TREATMENT AND ESTIMATE ASSOCIATED MANUFACTURING COSTS

To assess the annualized manufacturing costs associated with the optimum mine timber treatment system, a detailed cost analysis was conducted based on a model plant designed specifically for this function. The processes considered include only those directly associated with treatment of wood mine timber with fire retardants and preservatives for use in ground support; processes and associated costs for cutting, framing, boring, or transporting of timber were not included in the analysis.

The objective of the analysis was to determine the incremental treatment costs above and beyond those costs normally incurred for untreated timber.

Basic Assumptions and Cost Factors

It was assumed that the model treatment plant would be located in the proximity of a Western metal or nonmetal mine where square set timbering is the preferred method[3]. Timber would be cut locally, framed at a local mill, and would be shipped green to the treatment plant.

The annual tonnage of ore mined from such Western metal and nonmetal mines varies between 100,000 and 270,000 tons[3]; for this analysis, an hypothetical 200,000 tons/year was assumed for the mine to be serviced by the model treatment plant.

Timber consumption in such mines is typically 11 to 19 board feet per ton of ore mined; for this analysis a median 15 board-feet (bd-ft) per ton was used[3,4]. Therefore, timber requirements for the model mine were estimated to be 3 million bd-ft/year.

Assuming seven foot lengths of 12" x 12" timber, this 3 million bd-ft is equivalent to 36,000 timbers/year to be impregnated and coated. Total surface area to be coated was estimated to be approximately one million square feet/year.

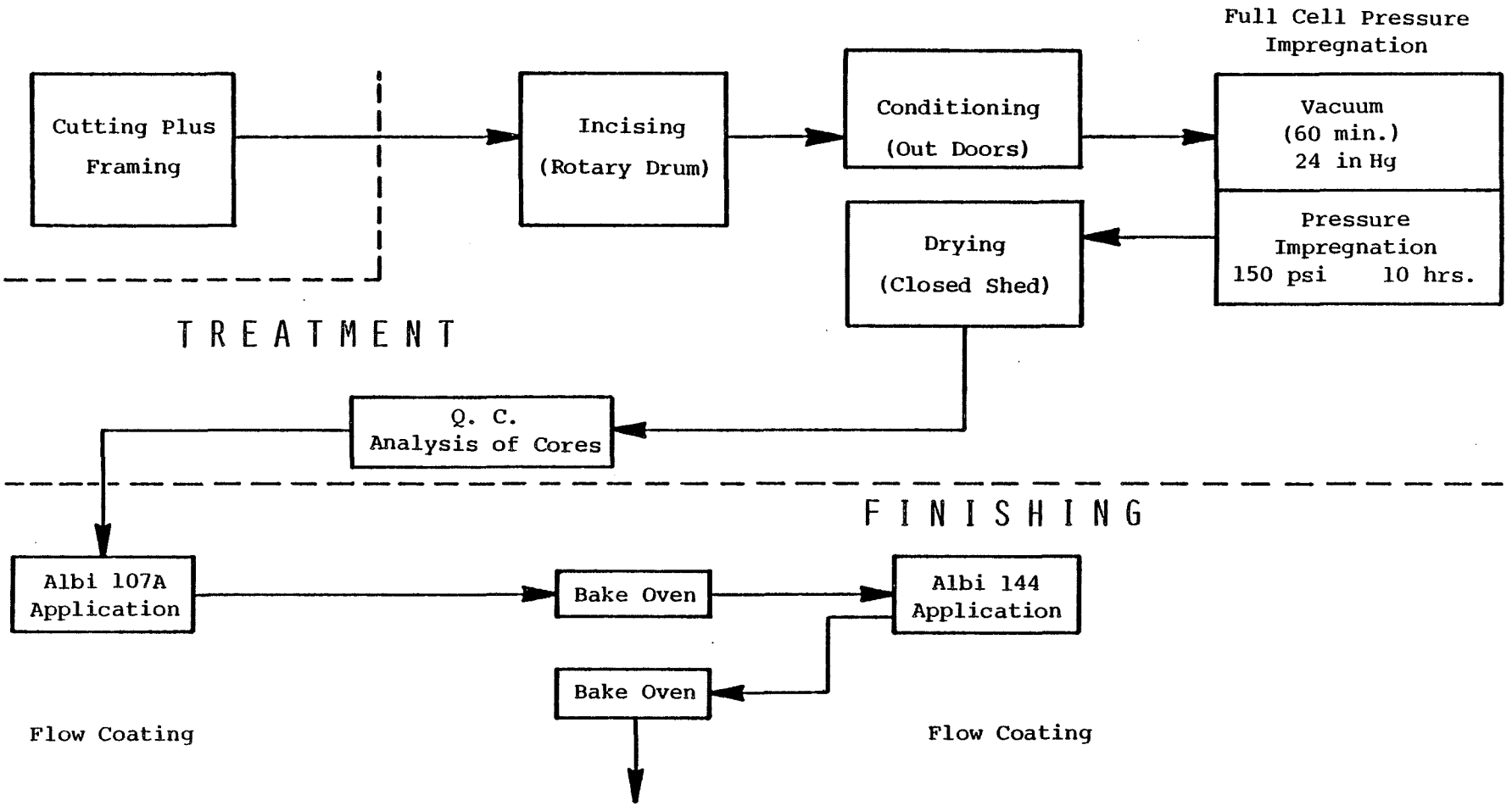
Impregnation Process

A process flow diagram for both treatment and finishing portions of the model plant appears in Figure 1. Since the structural timber to be treated in this process will likely be Douglas fir[3], incising has been included. Incising is commonly used both to prevent large checks during conditioning, and to enhance the depth of penetration during impregnation, and is generally required for impregnation of low permeability woods of this type[5].

The conditioning method of choice for this application is air drying in the open. While kiln drying is considerably faster, the energy requirements

FIGURE 1

PROCESS FLOW DIAGRAM



were judged to be too costly for this end use. Steaming, Boulton drying, and heating in preservative are also possibilities, but are used almost exclusively with oil-borne preservative; these processes would also be energy intensive.

Air drying normally requires six to twelve months; two acres of land would be adequate for this purpose.

Impregnation will be by the full cell method which is almost always used with aqueous systems[6]. The normal operating parameters will be as follows:

Batches or cycles: 3 to 4 per week	Timber size: 1 x 1 x 7 feet
Cell size: 22,000 gallons or 60 feet long x 8 foot dia.	Number of timbers: 720/week or 240/cycle
Packing density: 60%	Capacity: 20,000 bd-ft per cycle

Maximum working pressure: 200 psig

Typical cycle: Load - 2 hrs
Evacuate - 2 hrs (to less than 24 in. Hg)
Fill, pressurize and drain - 18 hours (150 psig)
Unload - 2 hrs

The pressure cell will be constructed from 3/4 inch plate consisting of 85% carbon steel and 15% 304 stainless steel cladding on the inside for corrosion resistance. The cell will be equipped with an hydraulically operated door and will be mounted out of doors on support saddles. Using fork lift trucks, timber to be treated will be loaded onto trams which can be wheeled into the cell on steel rails.

Treatment solution will be transferred to the cell from a 16,000 gallon storage tank (11.6 foot dia. by 21 foot high tank); this tank will also be mounted out doors and will be of glass reinforced polyester (FRP) construction.

A building, (20 foot x 20 foot) will be used for storage of salts and mixing of treatment solution. Solution will be prepared in a 2000 gallon open FRP tank (7 foot diameter x 7 foot high), and then transferred to the storage tank as needed.

The treated timber will be dried in a closed shed (50 foot x 100 foot) for approximately two weeks prior to coating. During this time, core samples will be taken to check for depth of penetration and assay retention.

Materials

A detailed breakdown of materials and costs can be found in the Appendix.

Assuming a depth of penetration of 0.4 inches[5], and a retention in the treated portion (assay retention) of 3.5 pounds/ft^3 Fyreprufe and 1.0 pounds/ft^3 ACC, the annual salt requirements are as follows:

Fyreprufe - 145,500 pounds

Acid Copper Chromate - 41,600 pounds

Labor

Direct labor will include one operator full time, a maintenance man half time, and a supervisor half time.

Impregnation Costs

The annualized impregnation costs for the model system appear on pages 26, 27, 30 and 31. Detailed backup for material costs appear in the Appendix.

Capital equipment costs are based on written and verbal quotations obtained from vendors except where indicated.

Coating Process

There are several industrial finishing processes that could be employed; the following lists the principal advantages and disadvantages of each:

Method	Advantages	Disadvantages
Automatic Spray	• no contamination of paint • comparatively low equipment cost	• low paint utilization (i.e. 30 to 50% overspray)
Dip	• good penetration of checks • fairly good paint utilization (70 to 80%) • fairly low capital cost	• fairly large quantities of paint required in tank with risk of considerable expense if spoiled • comparatively large floor space requirements • drips and runs common • possibility of paint contamination • large head space required above tanks • solvent loss from tank
Roll coating	• high production rates (probably overdesigned for this application)	• need multiple passes to do all four sides of • high capital cost

Method	Advantages	Disadvantages
Flow Coating	• less head space required than dip • highest paint utilization of the four methods (90 to 95%) • low solvent loss from coater • less paint "in process" than dip and, therefore, less potential spoilage • less floor space required than dip • good penetration of checks	• higher capital cost than dip or spray • although paint is filtered during recycling, there is more potential for contamination than with spray or roll • thinning likely required to get desired coating

Flow coating was selected largely because of its high paint utilization (90 to 95%); since a comparatively expensive coating system is being used ($22 to 23/gallon) economics will require maximum material utilization.

A process diagram for the coating operation appears in Figure 2; the steps of the operation are as follows:

. The wood is taken from the drying shed and loaded onto a monorail overhead conveyor

. Individual timbers travel longitudinally through a flow coater where a base coat of Albi 107A is applied. The flow coater has a self contained drain pan which catches paint drips and directs them back to the coater

. Some initial drying or "flash-off" of solvent takes place during transport of the timbers from the coater to the bake oven

. The coating is baked at 220°F for thirty minutes to drive off the remaining solvent; no curing takes place

. The timber passes through a second flow coater where a top coat of Albi 144 is applied

. After a brief flash-off, the top coat is baked thirty minutes at 220°F again simply to drive off residual solvent.

The normal operating parameters are as follows:

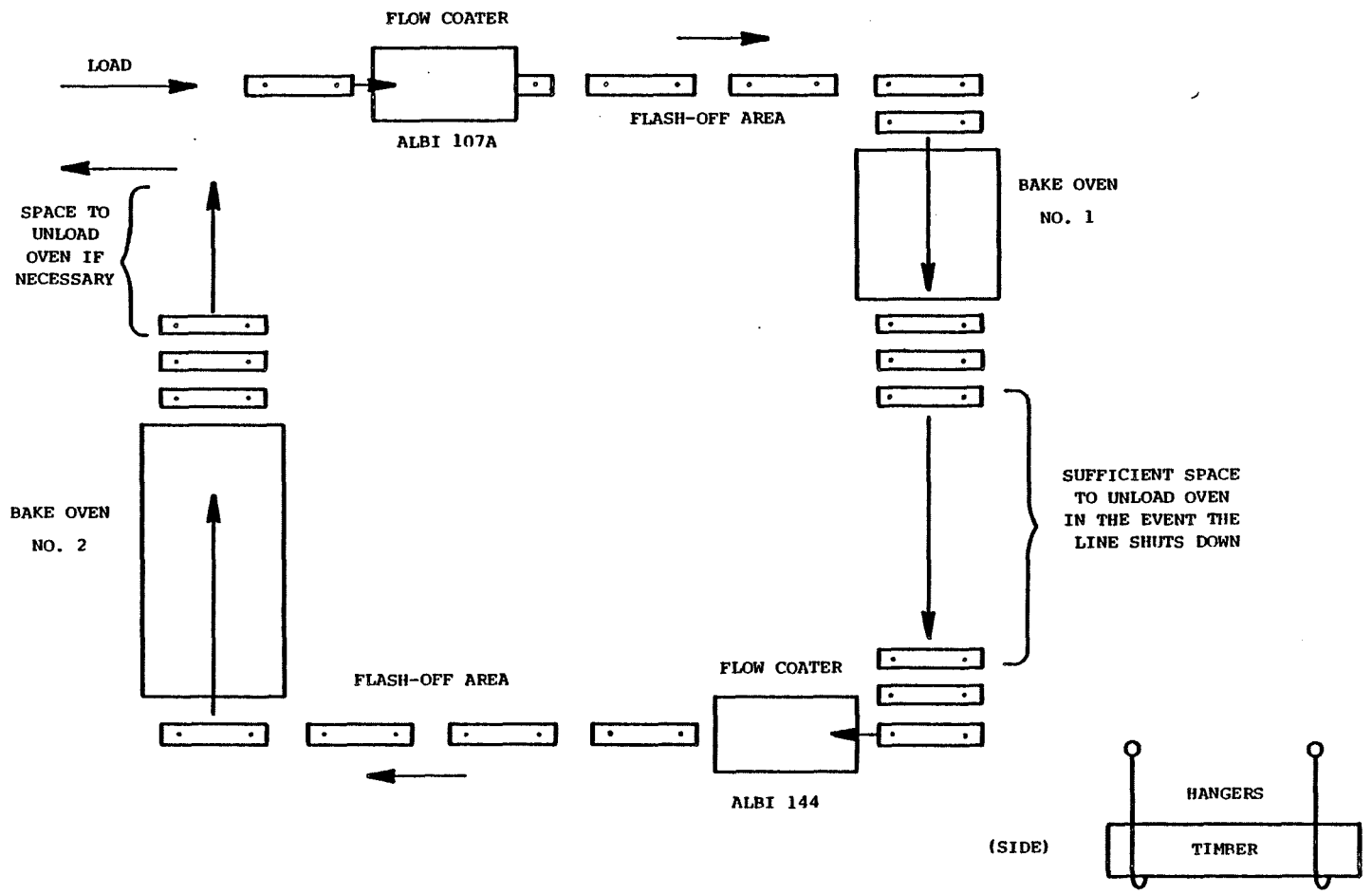
Conveyor Speed: through ovens - 1 ft/minute
through coaters - 4 ft/minute

Floor Space: 100 ft x 50 ft

Coating Weight: Albi 107A - 3.5 mils or approximately 300 ft^2/gallon
Albi 144 - 1.0 mils or approximately 450 ft^2/gallon

FIGURE 2

PROCESS DIAGRAM FOR FINISHING OPERATION



Paint Utilization: 90%

Design Rate: 30 timbers/hour or 900 ft^2/hr

Nominal Production Rate: 18 timbers/hr

Capacity Utilization: 60%

Oven Length: 30 feet

Bake Schedule: 30 minutes/220°F each oven

Materials

Paint and solvent requirements are as follows:

Albi 107A: 26.7 gallons per eight hour shift or 3,970 gallons/year
Assuming a 1.5 to 1 volume dilution, solvent to paint:
5,955 gallons/year of Xylene.

Albi 144: 17.8 gallons per eight hour shift or 2,660 gallons/year
Assuming a 1.5 to 1 volume dilution, solvent to paint:
3,990 gallons/year of mineral spirits

Solvents and coatings will be transferred to the coaters directly from 55 gallon drums using drum pumps.

Manufacturing Costs

Costs for both the impregnation as well as the coating process are presented on the following pages.

ANNUALIZED IMPREGNATION COSTS

Unit Operating Costs	Annual Total, $
Materials	
Fyreprufe	11,400
Acid Copper Chromate	19,400
Energy	
Gas (for drying shed)	5,000 (est.)
Electricity (inciser, mixers, vacuum/ pressure pump)	1,000 (est.)
Direct Labor	
One Operator @ $8.00/hr	16,000
Maintenance	
One person 1/2 time @ $9.00/hr	9,000
Allocated Overheads	
Supervision (50% of direct labor)	8,000
Fringes (35% of total labor)	11,500
Insurance (3% on total capital) (h)*	17,000
Property Taxes	
60 mils on $403,700 (b, d & e)*	24,200
TOTAL UNIT OPERATING COSTS	122,500 (a)

*Letters in parentheses identify cost items listed on the following pages in the right hand column.

CAPITAL COSTS

IMPREGNATION

Purchased Equipment	Total $	
Incising drum and conveyor	$ 67,000	
Pressure impregnation cell	194,000	
Carts and rails for moving timber	10,000	(est.)
Lift truck	9,000	(est.)
Mixing tank	1,700	
Transfer/storage tank	8,000	
Total Purchased Equipment	289,700	(b)
Development Costs and Engineering (15% of b)	43,500	(c)
Construction		
Floor space: Treatment building (20 ft x 20 ft) @ $35/ft^2	14,000	(d)
Drying shed (50 ft x 100 ft) @ $20/ft^2	100,000	(e)
Equipment Installation and Ancillary Equipment (35% of b)	101,400	(f)
Start-Up Costs		
Sixty (60) days of unit operation costs (16.7% of a)	20,400	(g)
TOTAL CAPITAL COST	569,000	(h)

ANNUALIZED COATING COSTS

Unit Operating Costs	Annual Total, $
Materials	
Albi 107A	93,500
Albi 144	59,400
Solvents	14,600
Energy	
Gas for ovens: 1600 KCF*/yr each at $4/KCF	12,800
Electricity	1,000 (est.)
Direct Labor	
Two operators @ $8.00/hr	32,000
Maintenance	
One person 1/2 time @ $9.00/hr	9,000
Allocated Overheads	
Supervision (25% of direct labor)	8,000
Insurance (3% of k, l, m and n) .03 x $436,000	13,100
Fringes (35% of total labor)	17,200
Property Taxes	
60 mils on k & m ($60 x 349)	20,900
TOTAL UNIT OPERATING COST	281,500 (j)

*KCF = thousand cubic feet

COATING PROCESS

CAPITAL COSTS

Purchased Equipment	Total, $
Flow Coaters (two)	60,000*
Ovens (two)	80,000*
Monorail Conveyor with Hangers (250 feet)	25,000*
Lift Truck	9,000 (est.)
TOTAL PURCHASED EQUIPMENT	174,000 (k)
Development Costs and Engineering (15% of k)	26,100 (l)
Construction	
Floor Space: 5000 ft^2 @ $35/$ft^2$	175,000 (m)
Equipment Installation and Ancillary Equipment (35% of k)	60,900 (n)
Start-Up Costs	
Sixty (60) days of Unit Operation Costs (16.7% of j)	47,000 (o)
TOTAL CAPITAL COST	483,000 (p)

*Estimates Based on Internal Sources

CAPITAL CHARGES (DEPRECIATION)

Impregnation

1)	Construction Items (d+e) Over 12 years	= $114,000	$ 9,500
2)	Development, Engineering, Equipment, Installation and Start-Up (b, c, f, g) Over 8 years	= $455,000	56,900
	TOTAL YEARLY DEPRECIATION		$66,400(i)

Coating

1)	Construction (m) Over 12 years	= $175,000	$14,600
2)	Development, Engineering, Equipment Installation and Start-Up (k, l, n, o) Over 8 years	= $308,000	38,500
	TOTAL YEARLY DEPRECIATION		$53,100(q)

ANNUALIZED IMPREGNATION COSTS

SUMMARY

Unit Operating Costs (a)	$ 122,000
Capital Charges (Depreciation) (i)	66,400
TOTAL ANNUALIZED COST	$ 188,400
Production (K bd. ft.*)	3,000
Cost/Unit ($/K bd. ft.)	$63.00

ANNUALIZED COATING COSTS

SUMMARY

Unit Operating Costs (j)	$ 281,500
Capital Charges (Depreciation) (q)	53,100
TOTAL ANNUALIZED COST	$ 334,600
Production (K bd. ft.*)	3,000
(ft^2)	1,000,000
Coating Cost/Unit ($/K bd. ft.)	$112
$/$ft^2$	$0.33

*K bd. ft. = thousand board feet

4: INSTALLATION OF A PILOT-SIZE PRESSURE IMPREGNATION CELL

The apparatus to be used for large-scale impregnation of mine timbers was built per Figure 3. Internal dimensions are 19 inches I.D. with a 37 inch working depth.

The pressure vessel was manufactured and delivered by International Fabricators after being hydrostatically pretested for 2 hours at 305 psig. To provide corrosion protection, the carbon steel vessel was spray painted inside and outside with two coats of Rustoleum 9373 orange epoxy primer and then spray painted inside with two additional coats of Rustoleum 9391 white epoxy primer using the manufacturer's recommended procedures. The pressure vessel was then located under an I-beam mounted chain hoist and bolted to the concrete floor.

Five stainless steel Whitey Ball valves, rated at 3000 psi @ $70^{\circ}F$ were plumbed per Figure 3 using 1/2" OD 316 S.S. tubing and fittings. Stainless steel braided and teflon-lined flexhose was used to connect hard plumbing to the removable pressure vessel cover.

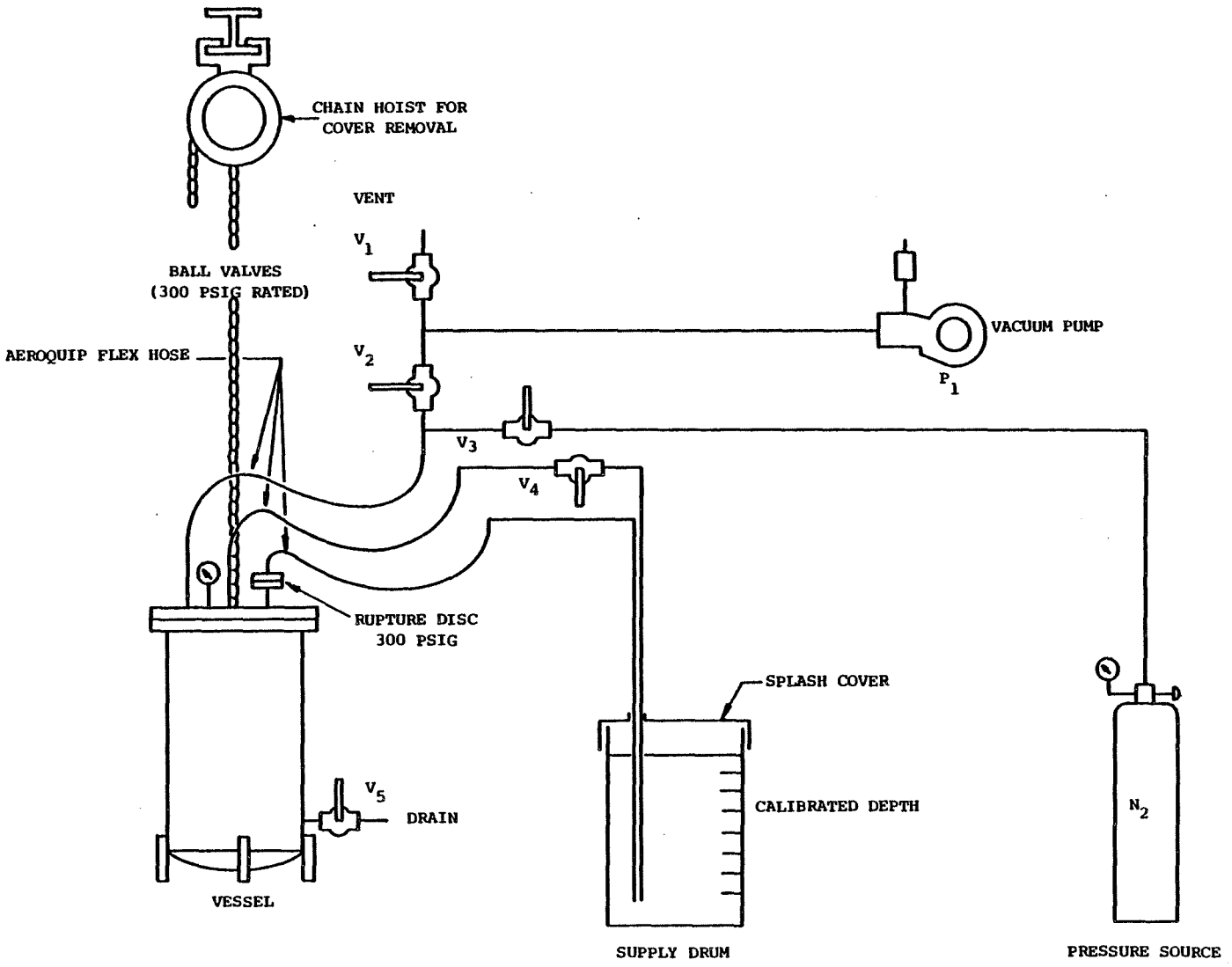
The supply drum is a standard open top steel drum lined with a corrosion resistant coating. Depth can be calibrated as the means of determining the amount of solution transferred to the pressure vessel and absorbed by the timbers.

Bottled nitrogen is the pressure source. Operating pressure and vacuum are indicated by a combination 300 psig pressure/vacuum gauge having stainless steel internals. Vacuum can be used to evacuate timber fiber as well as siphon impregnating solution from the supply drum. A rupture disk rated for 300 ± 20 psig will divert impregnating solution back to the supply drum in the event system overpressure occurs.

The cell is presently ready for pilot-scale impregnation of timber.

FIGURE 3

PILOT SIZE PRESSURE IMPREGNATION APPARATUS



5. LITERATURE SEARCH ON STENCH WARNING MATERIALS AND TECHNIQUES

Stench warning has been used to alert workers to the presence of fire or excessive heat in isolated locations of mines for over sixty years. The term "stench warning" refers to the heat or manually activated release of an odorific material designed to warn of fire when detected by smelling.

As early as 1918, valeric acid had been used in such a mining application, and between 1918 and 1920, the U.S. Bureau of Mines experimented with a wide variety of chemical compounds to increase the effectiveness of such systems[7]. By 1949, certain Canadian mines producing over 100 tons of ore per day were required by law to use stench warning devices which would introduce an odorant into the comprssed air lines of the mining equipment[8]. During the 1950's, the British Safety in Mines Research Establishment (SMRE) experimented with methods to increase the effectiveness of existing mechanical means of introducing stench agents into mines[9].

In related applications, odorants have been added to natural gas for detection purposes for over fifty years. Stench warning devices have also been used to alert workers to machinery bearing overheating, especially in railroad applications[9]. In a much more recent study, stench agents were investigated regarding their usefulness in detecting the presence of pesticides in sprayed fields[10].

Odorant Compounds

Table 5 details the wide variety of compounds which have been investigated as stench warning materials over the past sixty years. Compounds have been grouped by chemical type and, generally in order of increasing molecular weight. Each chemical category is summarized briefly below:

- Mercaptans

Mercaptans, or thiols, are the sulfur analogs of alcohols. The lower molecular weight mercaptans have a long history of use as stench warning agents in mines and as natural gas odorants. Low odor detection thresholds combined with relative non-toxicity in low concentrations have made these compounds ideal in these applications. Most of the mercaptan information in Table 5 is from manufacturers' data sheets. Principal producers of aliphatic thiols are Pennwalt and Phillips Petroleum.

- Sulfides

Sulfides are bivalent sulfur compounds which are analogous to ethers. Most sulfides have distinctively foul sulfurous odors, which has led to investigation of their use as stench agents. Sulfides tend to be more toxic than mercaptans, especially the lower molecular weight compounds (hydrogen sulfide is quite poisonous). The primary interest in sulfides for stench applications has been their use as odorants for natural gas. Much of the

sulfide information in Table 5 comes from work done by the Bureau of Mines prior to 1930[11].

- Musks

Musks are both naturally occurring and synthetic compounds used as fixatives for perfumes. All are nontoxic, very high boiling, and have very low perception thresholds and persistent musky odors. However, unlike the sulfur compounds, musks lack the pungency necessary for rapid recognition. Most of the compounds listed were evaluated in pesticide warning applications[10].

- Fragrances

This is the largest category of odorific compounds, most of which are naturally occurring as fragrances or flavorings. In concentrated form, many of these compounds are high boiling oils with low odor perception thresholds. All are of a very low order of toxicity. Although highly odorific, these compounds may show a tendency to "cling" to a substrate and fail to propagate as an effective warning agent should. In addition, most compounds in this category have pleasant odors and are therefore less likely to provide rapid recognition as an emergency warning signal.

- Others

These are compounds that did not fall within the major groupings of the other odorants listed. Thiophene and tetrahydrothiophene have been used as natural gas warning agents. Skatole, a heterocyclic nitrogen compound, has been used in a variety of applications including fire, fuel gas, and pesticide warning systems. Skatole appears to be unique in that it combines repulsive odor, high boiling point, low detection threshold, and water solubility.

Problems with Odorant Compounds

The ideal compound for use in a fire stench warning system would be one which is relatively non-volatile at room temperature, yet becoming increasingly volatile at or near temperatures encountered in a fire. Such a compound would also possess a low odor detection threshold concentration and have an odor capable of evoking a sharp human response. Other considerations would be flammability, toxicity of the odorant compound and its combustion products, permanence of the unactivated odorant, and propagation ability of the odorant once released. Several of these specific problems are discussed below in relation to the odorant compounds listed in Table 5.

- Odor Detection Threshold

All compounds selected for inclusion in Table 5 possess low odor detection concentration limits. This is a consideration of major importance for any stench warning compound, since an effective material must be detectable at extreme dilutions in ventilation air streams (e.g. 2,000 to 10,000 cfm).

TABLE 5: ODORANT COMPOUNDS WITH PAST HISTORY OF USE IN STENCH WARNING APPLICATION INVESTIGATIONS

Compound	Nature of Odor	Molecular Weight	Boiling Point (°C)	Odor Threshold (ppb v/v)	Flammable	Water Soluble	Toxicity 1 Physiological Effects
• Mercaptans							
ethyl mercaptan	decayed cabbage	62	34	0.26	Yes	sl	low toxicity/nauseating
n-propyl mercaptan	onions	76	66	1.6	Yes	sl	low toxicity/nauseating
isopropyl mercaptan	---	76	51	2.0	Yes	sl	low toxicity/nauseating
n-butyl mercaptan	skunk	90	96	0.5	Yes	sl	low toxicity/nauseating
t-butyl mercaptan	skunk	90	62	---	Yes	sl	low toxicity/nauseating
amyl mercaptan	skunk	104	120	0.43	Yes	No	low toxicity/nauseating
allyl mercaptan	garlic	74	67	1.5	Yes	sl	low toxicity/nauseating
benzyl mercaptan	disagreeable	124	194	2.6	Yes	sl	mildly irritating
crotyl mercaptan	skunk	128	---	0.12	Yes	sl	low toxicity/nauseating
• Sulfides							
hydrogen sulfide	rotten eggs	34	- 41.3	2.0	Yes	sl	poisonous
methyl sulfide	decayed vegetation	62	36	3.7	Yes	No	nauseating
ethyl sulfide	decayed vegetation	90	92	2.8	Yes	No	nauseating
n-propyl sulfide	foul; becomes ethereal	118	142	11	No	No	nauseating/congestive
n-butyl sulfide	sulfurous; foul	146	182	15	No	No	nauseating
isoamyl sulfide	foul, ethereal	174	---	3.0	No	No	nauseating
benzyl sulfide	ethereal	214	m. 49	6.0	No	No	none
diphenyl sulfide	ethereal	186	296	0.34	No	No	evokes chocking sensation
allyl sulfide	garlic oil	114	139	0.14	No	No	nauseating/irritating
allyl disulfide	garlic; putrid	146	---	1.2	No	No	nauseating/irritating
• Musks							
2,4,6-trinitrot-butyl xylene	like natural musk	283	m. 96-7	0.001	No	No	non-toxic
11-oxahexadecanolide	like natural musk	256	m. 35	---	No	No	non-toxic
musk ambrette	like natural musk	268	---	---	No	No	non-toxic
musk xylene	like natural musk	297	---	---	No	No	non-toxic
musk ketone	like natural musk	294	---	---	No	No	non-toxic
3-methylcyclopentadecanone	natural musk	238	328	---	No	sl	non-toxic

Table 5 - (Continued - 2)

Compound	Nature of Odor	Molecular Weight	Boiling Point (°C)	Odor Threshold (ppb v/v)	Flammable	Water Soluble	Physiological Effects
• Fragrances							
3-methoxypyrazine derivatives:							
2-hexyl-	like fresh bell pepper	194	---	0.001	---	---	likely non-toxic
2-isopropyl-	like fresh bell pepper	152	---	0.002	---	---	likely non-toxic
2-isobutyl-	like fresh bell pepper	166	---	0.002	---	---	likely non-toxic
2-propyl-	like fresh bell pepper	152	---	0.006	---	---	likely non-toxic
phenol ether derivatives:							
anethole	anise	148	m. 23	---	No	No	likely non-toxic
vanillin	vanilla	152	285	0.016	No	Yes	non-toxic
eugenol	clove	164	255	3.5		No	non-toxic
isoeugenol	clove	164	266	---		sl	non-toxic
ethyl vanillin	vanilla	166	m. 77	---		sl	non-toxic
diphenyl ether	ethereal	170	259	0.001	No; FP= 115°	No	---
1,7,7-trimethylbicyclo [4.4.0]-decane derivatives:							
-3-one	floral	195	87	0.001			
-3-formate	floral	224	85	0.01			
-3-acetate	floral	238	90	0.01			
-3-acrylate	floral	250	86	0.01			
-3-propionate	floral	252	100	0.02			
-3-butyrate	floral	266	115	0.05			
lactones and derivatives							
γ-decalactone	like peach	170	281	---			likely non-toxic
γ-undecalactone	like peach	184	286	---			likely non-toxic
γ-dodecalactone	like peach	198	---	---			likely non-toxic
α-(2-hydroxycyclohexyl methyl) butyrolactone	peppermint	196	203	---			likely non-toxic
esters							
isoamyl acetate	banana	130	142	3.3	Yes	sl	minor throat irritation
methyl anthranilate	grape	151	m. 25	0.65		sl	non-toxic
isoamyl isovalerate	apple	172	192	6.6		v. sl.	non-toxic
benzyl benzoate	aromatic	212	323	---		No	irritant

Table 5 - (Continued - 3)

Compound	Nature of Odor	Molecular Weight	Boiling Point (°C)	Odor Threshold (ppb v/v)	Flammable	Water Soluble	Physiological Effects
benzyl salicylate	pleasant	228	368	---		sl	likely non-toxic
benzyl cinnamate	balsam	238	350	---		No	likely non-toxic
β-phenylethylphenylacetate	rose-hyacinth	240	324	---		No	likely non-toxic
terpenes							
citronellol	rose, geranium	156	225	---		v. sl.	non-toxic
menthol	peppermint	156	212	---	No	sl.	non-toxic
β-ionone	cedar or violet	192	250	0.013	No	v. sl.	non-toxic
α and β-santalol	sandalwood	220	302	---		No	non-toxic
miscellaneous							
2-phenylethanol	floral; rose	122	220			sl.	non-toxic
coumarin	like vanilla	146	298	0.28	No	sl.	non-toxic
2-methoxynaphthalene	floral	158	272	0.12		No	
1-(phenylethoxy) adamantane	floral	256	---	---			likely non-toxic
• Others							
thiophene	benzene-like	84	84.4		Yes	No	
tetrahydrothiophene	aromatic; sulfurous	88	120	1.3	Yes	No	
skatole	decayed flesh; putrid	131	265	0.3		Yes	
indole	---	117	254	---		---	

Explanations:

m. - denotes melting point of a solid compound
FP - flash point (open cup)
sl. - slightly
v. sl. - very slightly
ppb v/v - parts per billion, volume basis

- Volatility

The volatility of an odorant will give some indication of its effectiveness as a warning agent. Volatility will increase with temperature, a desirable property in some cases since high volatility at or near the combustion temperature of wood is required of any fire activated stench warning. Table 6 shows the tendency toward volatilization of several alkyl mercaptans at room temperature and 230°C reflected by the vapor pressures of the compounds. Higher vapor pressures indicate a higher degree of volatility.

TABLE 6

VAPOR PRESSURES OF SELECTED MERCAPTANS[12]

Compound	Molecular Weight	Vapor Pressure mm Hg at 25°C	Vapor Pressure mm Hg at 230°C
methyl mercaptan	48	(2000)	---
ethyl mercaptan	62	520	---
t-butyl mercaptan	90	175	---
n-butyl mercaptan	90	45	---
n-hexyl mercaptan	118	(6)	(4600)
t-nonyl mercaptan	160	(1.5)	(1800)
t-dodecyl mercaptan	202	---	575
n-dodecyl mercaptan	202	---	400

(Extrapolated values in parentheses)

As with most compounds, higher molecular weight produces a less volatile compound at room temperature. This indicates that a compound such as hexyl mercaptan (MW 118) would be only moderately volatile at room temperature, but very volatile at 230°C, just below the combustion temperature of wood.

The higher molecular weight mercaptans may be less volatile at room temperature, but the pungency of their odors is greatly reduced. Whereas ethyl mercaptan is highly odorific, giving an easily recognizable smell of rotten vegetation, dodecyl mercaptan is a much more subtle, musky odor. All of the musk compounds have high molecular weight, low volatility at room temperature, and very low odor detection thresholds, but the musk odor is unobtrusive and would possibly take longer to recognize and respond to. All of the higher molecular weight sulfur compounds and musks appear to have this type of characteristic odor which could prove difficult to detect quickly in a mine.

- Permanence

Permanence of stench agents in the unactivated condition is necessary for both economic reasons (replacement costs) and to avoid the problem of accidental release and false alarms. The permanence of any odorant is closely related to volatility, with the less volatile compounds being longer lasting.

Attempts have been made to lower the volatility of odorant compounds by methods such as:

(1) Higher Concentrations

Obviously, larger amounts of an odorant will last longer, but this is only a temporary means of increasing permanence.

(2) Use of Fixatives

Odorants can be admixed with other compounds which act to retard the evaporation of the stench agent. Typically, these are higher boiling compounds or polymer solutions which are miscible with the odorant. Both mineral oil and ethyl cellulose polymer solutions have been investigated in this application.

(3) Physical Containment

Volatile odorants can be effectively sealed in containers and released when desired by simply rupturing the container. Stench warning systems using the volatile lower molecular weight mercaptans operate in this manner. Various physical containment techniques are described on pages 41 through 47.

- Propagation Properties

No matter how useful an odorant may be in evoking rapid recognition, the compound will only achieve its maximum effect if propagation is widespread and many people are alerted to the danger of fire. Normally, this would not appear to be a problem, as air volume flow rates may be as high as 2,000,000 cfm in a main shaft[13]. However, some odorants have shown a tendency to cling to substrates in and around the area of release[14], particularly in coal mines.

Mercaptan manufacturers detail procedures using activated charcoal for deodorizing empty mercaptan drums. For this reason, mercaptans cannot be expected to propagate past coal faces in a mine, as the compounds are adsorbed onto the strata, with the coal acting much like activated charcoal.

- Flammability

A compound is generally considered flammable if it has an open cup flash point below 100°F. Materials with higher flash points are classified as combustible. Nearly any organic compound will burn if heated to a high enough temperature, but combustible odorants would be preferable to flammable compounds even when the odorant is used in relatively small quantities.

Most of the organosulfurs are flammable, especially the lower molecular weight compounds. In past usage as odorants for natural gas, this has been a benefit, but in stench fire warning systems using mercaptans, flammability

has always been a major concern. At the point of release, the initial concentration of flammable odorant can be quite high. If the system is thermally activated, the release location would be at the source of the heating and a dangerous situation could exist.

Most currently available commercial systems introduce a mercaptan-fluorocarbon mixture into a mine's compressed air lines. The fluorocarbon serves as a propellant for the odorant but also reduces the flammability of the compound. The danger of explosion of odorant vapors is also lessened because almost all of these systems are manually activated at a central location some distance from the fire itself.

- Toxicity

Odorant toxicity must be looked at from two different viewpoints--that of the odorant compound itself, and that of its combustion products.

Most odorant compounds listed in Table 5 are relatively non-toxic. The only concern may arise with the lower sulfides (hydrogen sulfide is poisonous) and high concentrations of mercaptans. Musks are not considered toxic, and many of the frangrances listed are commonly used in cosmetics and foods. Care was taken in excluding from the table most compounds known to be toxic. Toxicity of any odorant itself is probably not a major concern considering the concentration levels that would be encountered in an activated stench warning system.

The other more serious concern is the toxicity of combustion products of an odorant released at the source of a fire. Mercaptans evolve sulfur dioxide and hydrogen sulfide on combustion, both of which are quite toxic. However, dilution of such compounds to low concentrations may reduce this risk substantially.

STENCH WARNING TECHNIQUES

Current Commercial Systems

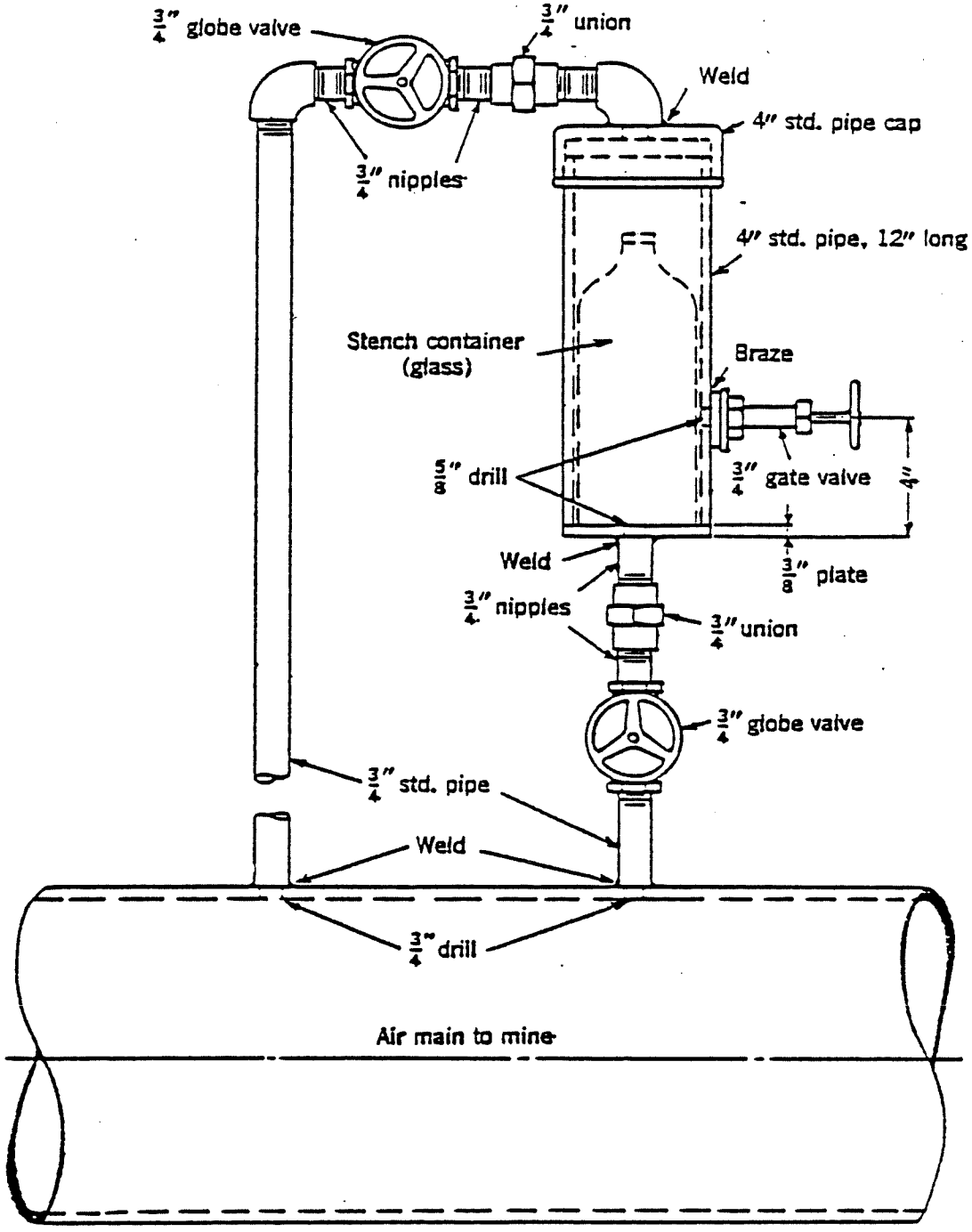
All stench warning systems currently in use in the United States introduce an odorant (generally an ethyl mercaptan-Freon mixture) into mine ventilation, compressed air lines, or both. The systems are manually activated when notice of a fire is given. The point of activation is generally some distance from the actual fire, possibly even on the surface outside the mine. The main difference between these systems is the method of odorant introduction into the air lines or ventilation systems. The most common techniques are outlined below.

- Vial Breakage

Figure 4 shows a stench injection system of this type. The odorant is supplied in a sealed glass vial or bottle and is released by puncturing the container to allow the odorant to escape. Odorant compounds can be purchased presealed in glass eliminating handling problems. The sealed unit is simply

FIGURE 4

STENCH INJECTOR SYSTEM



placed in the injection loop as shown where it remains until activated. This type of injection system tends to be less reliable than some of the others due to the unpredictability of glass breakage patterns and valve failure due to corrosion. Instances have been noted where the top of the vial broke leaving the major portion of the container intact, resulting in poor release of the odorant. Also, the ethyl mercaptan stench agent often used in these systems is quite corrosive and residual odorant may severely damage the injector valve system. The unit also suffers from the drawback of not giving any visual indication of proper activation since the vial is hidden from direct view.

- Manual Introduction of Liquid Odorant

In this type of system, liquid odorant is poured into the injection loop and then released by the manipulation of various valves. A typical device of this kind is shown in Figure 5. This type of unit is not commonly used because it requires direct handling of the stench liquid by mine personnel. However, these devices tend to be more reliable than vial breakage systems, mainly because the amount of odorant injected can be observed.

- Pressurized Canister Injection

Pressurized canister or cartridge systems have widespread use in the U. S. Mines. As shown in Figure 6, they consist of a pressurized canister containing odorant and propellant and a simple valve system to permit injection into air lines or ventilation systems. Advantages are simplicity of operation and ease of handling of the prepackaged stench agent by mine personnel.

Experimental Systems

Various other methods of releasing odorant compounds have been explored in efforts to improve on current techniques. The major problems with systems now in use are that the rate of release of the odorant is not controlled and activation of the system must be done manually. Some possible solutions to these problems are described below.

- Metered Injection Techniques

Foster-Miller Associates, Inc. of Waltham, Mass., describe the development of metered odorant injection systems in their report, "Upgrade Stench Fire Warning System - System Development and Prototype Tests"[13]. They describe injection techniques using metering nozzles (with and without pressure balancing) and variable volume metering pumps to control the volume and rate of odorant injection into compressed air lines or ventilation. This type of metered injection enables the stench agent to be released uniformly without an excessive buildup of odorant at the release site.

- Stench Capsules

Figure 7 shows a cutaway view of a stench capsule developed by SMRE in Great Britain during the 1950's. The design is similar to that used for capsules designed to protect railroad engine wheel bearings. The unit itself is

FIGURE 5

STENCH INJECTOR DEVICE

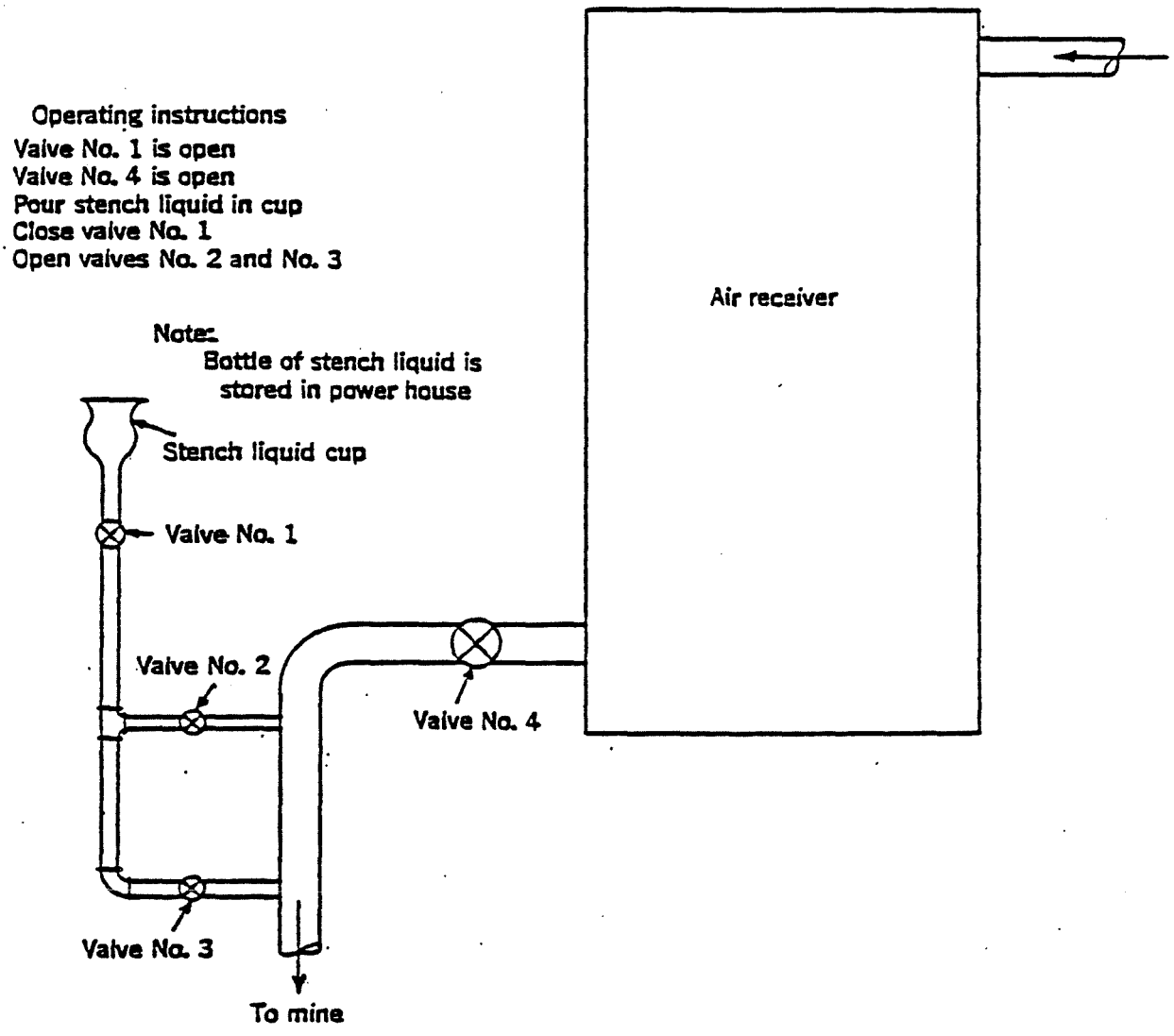


FIGURE 6

TYPICAL STENCH INJECTION SYSTEM
USING PRESSURIZED CANISTER

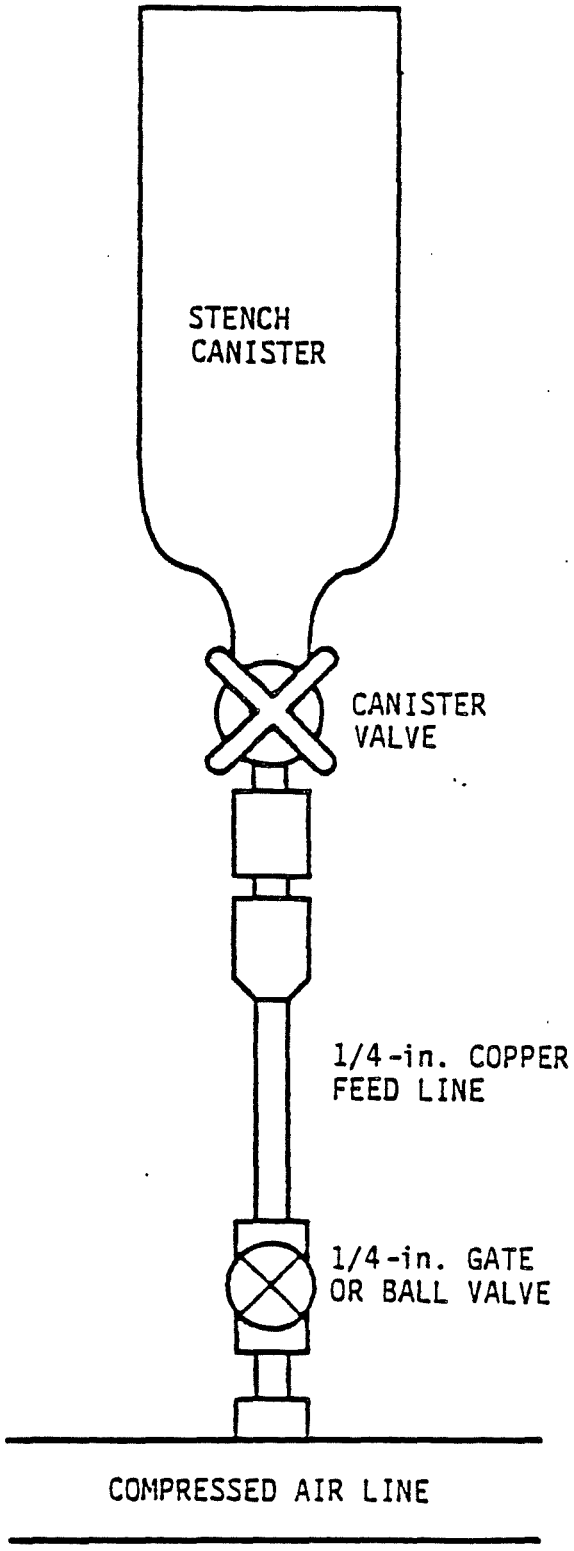
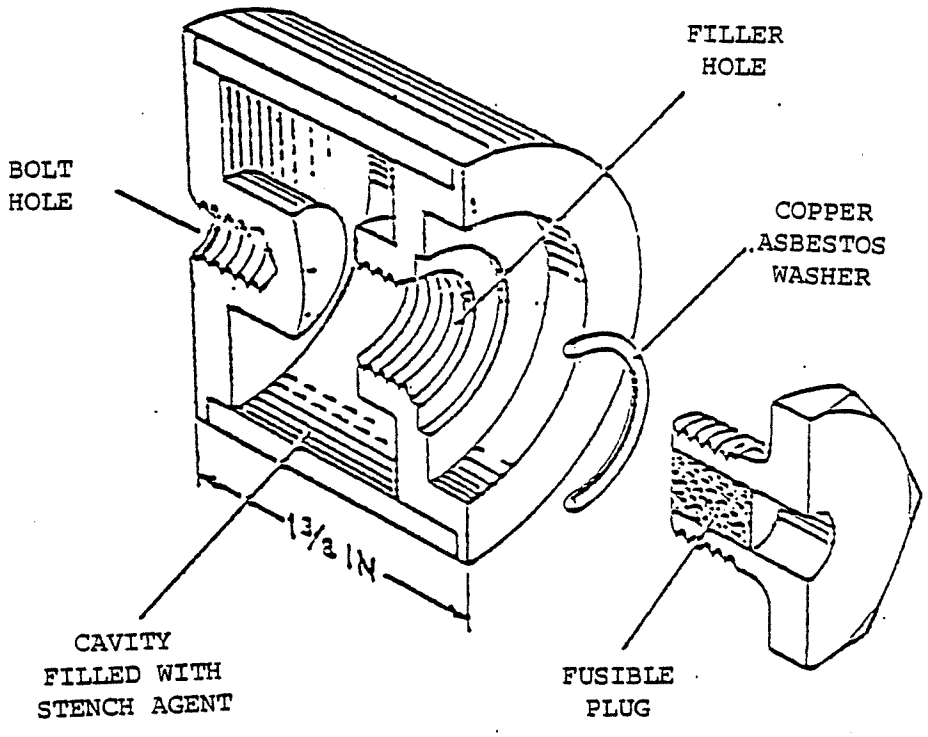


FIGURE 7

HEAT-ACTIVATED STENCH CAPSULE
WITH FUSIBLE PLUG



a small steel cylinder containing 20-30 ml of odorant. The capsule is sealed with a fusible plug made from a low melting metal alloy. In the event of a heating or fire, the plug would melt, releasing the stench agent. The major advantage of this type of system is that activation is automatic. Current stench warning systems are manually activated and this necessitates a delay from the time a fire is detected until a worker can activate the alarm. A stench capsule is activated by the fire itself, so no delay between fire detection and system activation occurs.

This type of system suffers from some major drawbacks. As with other current systems, odorant release is uncontrolled and very high stench agent concentrations could build up at the point of release. Also, and more importantly, the point of release is at or near the fire itself. This could easily create an explosion hazard with flammable odorants such as ethyl mercaptan. A fluorocarbon propellant could reduce this risk, but the explosion potential with such a system is still a major concern. Any odorant used in such a system would need to be non-flammable.

- Mine Timber Treatment

The idea of treating mine timber with odorant materials does not appear to have received much attention. It may be possible to either apply agent containing coatings or to impregnate stench agents directly into mine timber along with fire retardant and preservative treatments. Most likely candidates would be musks, fragrances, or skatole, which is water soluble. Some organosulfur compounds might also be suitable for this application, especially thioesters and related compounds which could hydrolyze or decompose to odorific products.

The problem of permanence would need to be addressed, but it is likely that fixatives, mine timber coatings, or microencapsulation techniques could help solve this problem.

6. TREATMENT CONCEPTS DEVELOPMENT FOR SHORT-RANGE STENCH HEATING WARNING SYSTEMS

Introduction

Based on a review of materials and concepts previously investigated in stench warning applications, several classes of compounds appear suitable for use in short-range heating warning systems. Organosulfur compounds, fragrances, and some heterocyclic nitrogen compounds seem best suited as stench warning materials for direct application to mine timber.

Mercaptan odorants will evoke rapid human response at low concentrations due to their characteristic sulfurous odor and low odor detection thresholds. Flammability and toxicity are probably minor considerations due to the low concentrations of odorant required. The most significant problem with mercaptans is that of permanence in the unactivated state and much of the present concept development is directed toward solving this problem by various physical and chemical containment techniques.

Fragrances may also prove useful as warning agents in heating applications. Their pleasant odors should be readily recognizable and easily distinguished from the mercaptan stench commonly used in central mine fire warning systems. The unique odor would enable mine workers to quickly recognize a local heating alarm, investigate the nature of the heating, and then activate the main warning system only if necessary. As a class of compounds, fragrances have higher molecular weights and are considerably less volatile than mercaptans. Permanence could be further increased by the use of fixative materials.

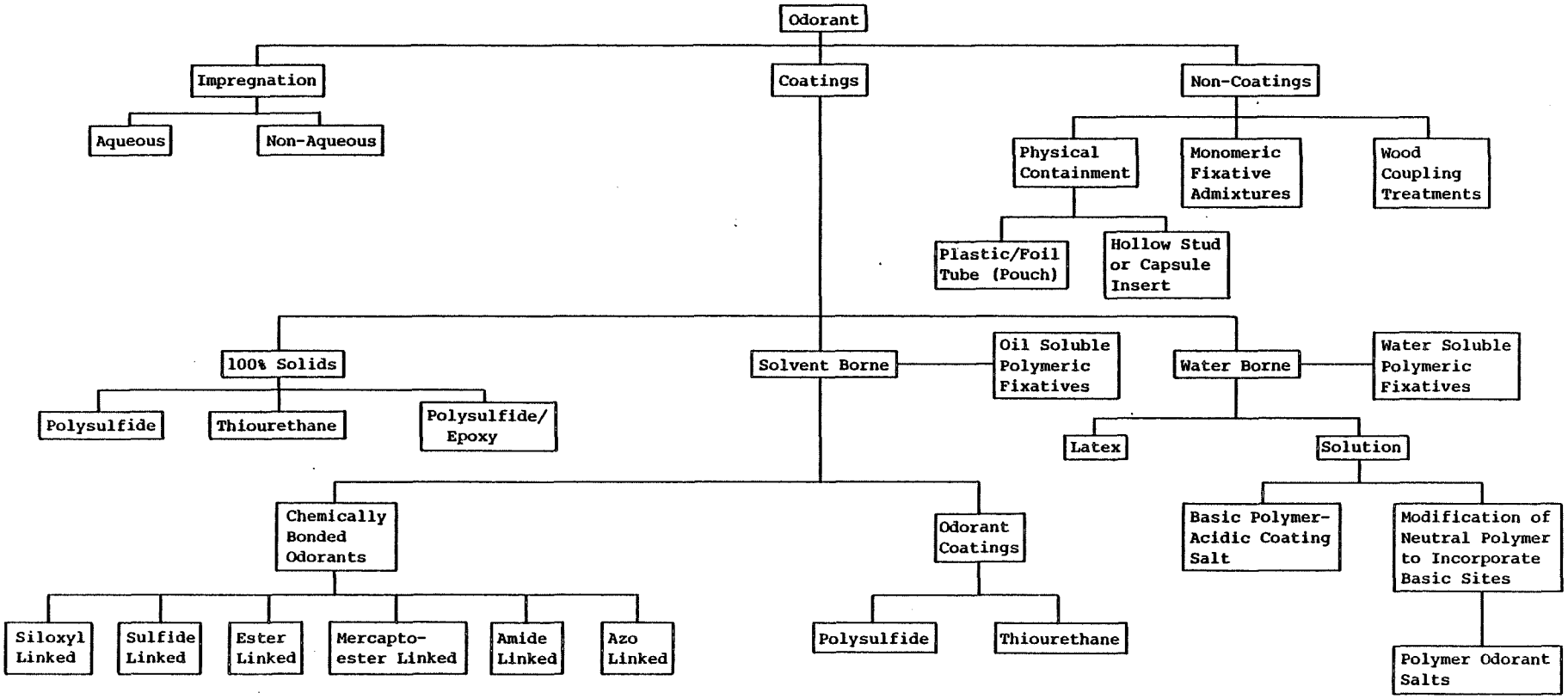
Indole, skatole, and other heterocyclic nitrogen compounds also offer potential as short-range heating warning agents. These compounds have a distinctly repulsive odor, and water solubility might make them candidates for timber impregnation treatments.

The concept development effort was directed toward coatings and physical containment techniques, primarily due to simplicity and ease of application. Impregnation of mine timber was also considered, but the effectiveness of an impregnated odorant in a heating warning system is questionable. Topically applied stench agents would receive greater exposure to heating in the event of a fire making heat activated coating more effective than an impregnated material. Several non-coating techniques were also considered where materials would be applied to the surface of a mine timber, but would not have the physical integrity to be considered a coating.

In addition, several methods of physical containment were considered where the odorant would be sealed in a unit that would then be attached to the mine timber. In the event of a fire, heat would disturb the seal on a device of this type, allowing the release of odorant to act as a warning signal. The various warning system concepts have been categorized in Figure 8 and discussed as follows:

FIGURE 8

CONCEPT DEVELOPMENT
STENCH HEATING WARNING SYSTEMS



Solvent Borne Coatings

Solvent borne polymeric coatings may provide a suitable substrate to which certain types of mercaptans could be chemically bound. This would increase the permanence of the odorant by in effect raising its molecular weight. Hopefully, the reaction would be reversible at elevated temperatures, allowing the odorant to function as a heating warning agent. In order to chemically bind an odorant to a polymer backbone, it is necessary to use the reactivity of either the mercaptan group or some other functional group that may be present in the odorant compound. A wide variety of multifunctional sulfur compounds are available from suppliers.

Odorant systems of this type can be classified according to the nature of the chemical bond between the coating material and the odorant. Several possible coupling linkages are described in Table 7 along with the necessary odorant functionality to chemically react it with a particular coating type.

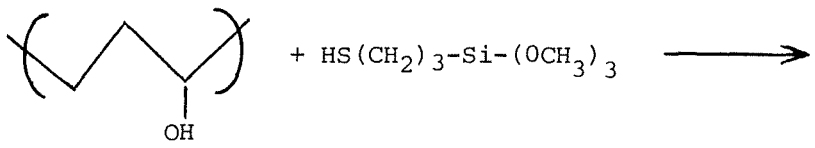
TABLE 7

ODORANT/COATING BOND DESCRIPTIONS

Nature of Bond	Coating Functionality Required	Odorant Functionality Required
Siloxyl	Hydroxyl	Siloxane
Sulfide	Epoxy	Mercapto
Ester	Carboxyl	Hydroxyl
	Hydroxyl	Carboxyl
Amide	Carboxyl	Amine
	Amino	Carboxyl
Azo	Amino	Aryl Hydroxyl
Mercaptoester	Carboxy	Mercapto

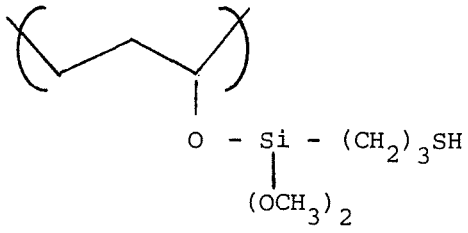
- Siloxyl Linked Odorants

A coating containing free hydroxyl groups could be bound to an odorant with siloxane functionality. A mercaptosilane would possibly be odorific enough to serve as a warning agent in this type of system. The reaction of a mercaptosilane with a hydroxyl functional coating is represented as follows:



hydroxyl functional coating

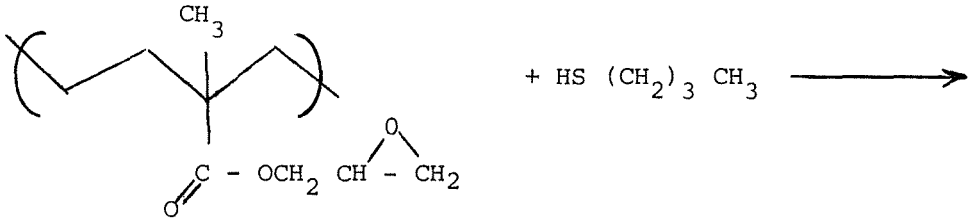
mercaptopropyl trimethoxysilane (Dow Corning Z-6062)



The reaction should proceed quite readily, especially when catalyzed with an amine.

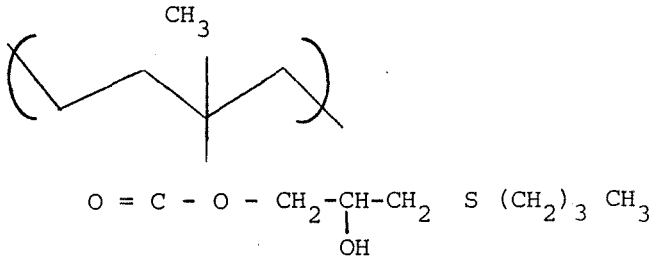
- Sulfide Linked Odorants

Coatings with epoxy functionality could react with an odorant containing active hydrogens. The mercapto hydrogen would be suitable in this type of reaction.



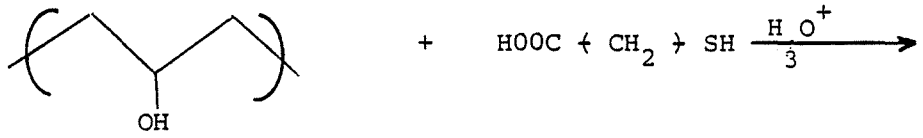
acrylic copolymer with glycidyl methacrylate

butyl mercaptan



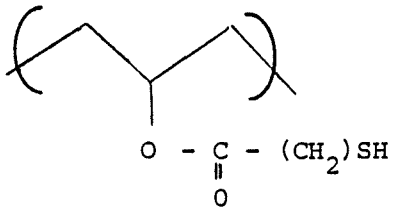
- Ester Linked Odorants

Coatings with carboxyl or hydroxyl functionality could be made to react with sulfur compounds with free carboxyl or hydroxyl groups to form ester linkages.



hydroxyl functional coating

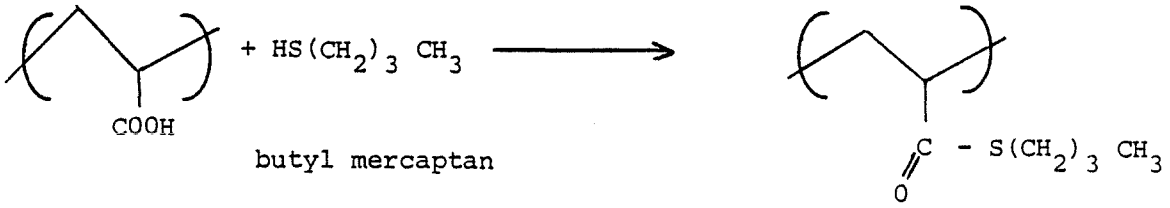
thioglycolic acid



The reverse reaction (hydrolysis) can be acid or base catalyzed, and the use of a compound that becomes acidic on heating such as ammonium sulfamate, might serve to catalyze the release of odorant at elevated temperatures.

- Mercaptoester Linked Odorants

It may be possible to react a mercaptan to a carboxyl functional polymer to form a mercaptoester. Reactivity of various odorants would probably vary, depending on the structure of the particular mercaptan used. Such a reaction can be illustrated by the following:



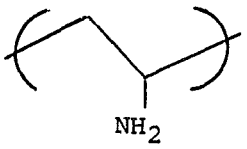
butyl mercaptan

carboxyl functional polymer

The reaction product could also be considered a sulfide and would likely decompose on heating to regenerate the bound mercaptan.

- Amide Linked Odorants

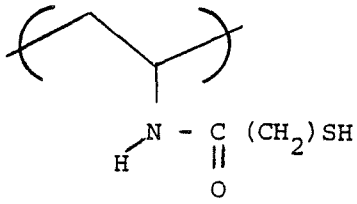
An amino functional polymer could be reacted with a carboxyl functional odorant to produce an amide link.



amino functional coating

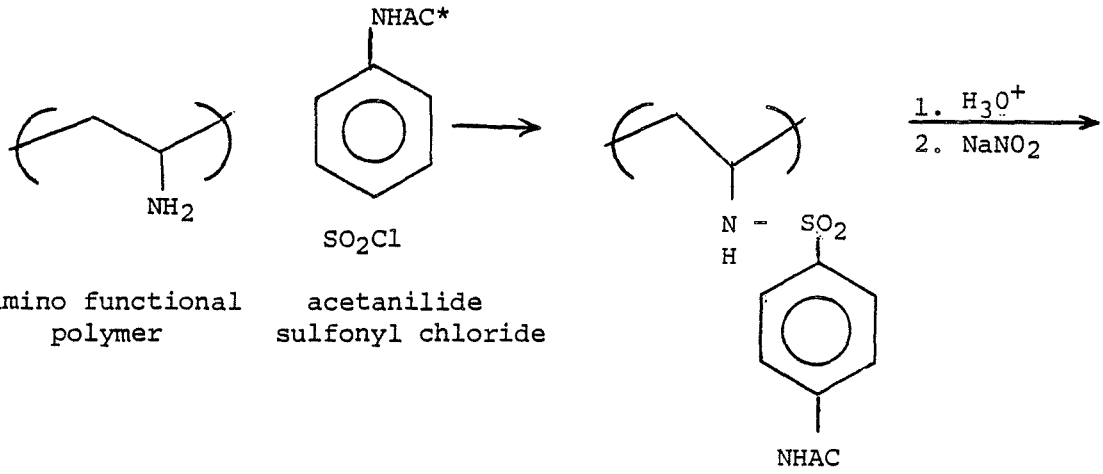
+ $HOOC(CH_2)SH$ ⟶

thioglycolic acid



- Azo Linked Odorants

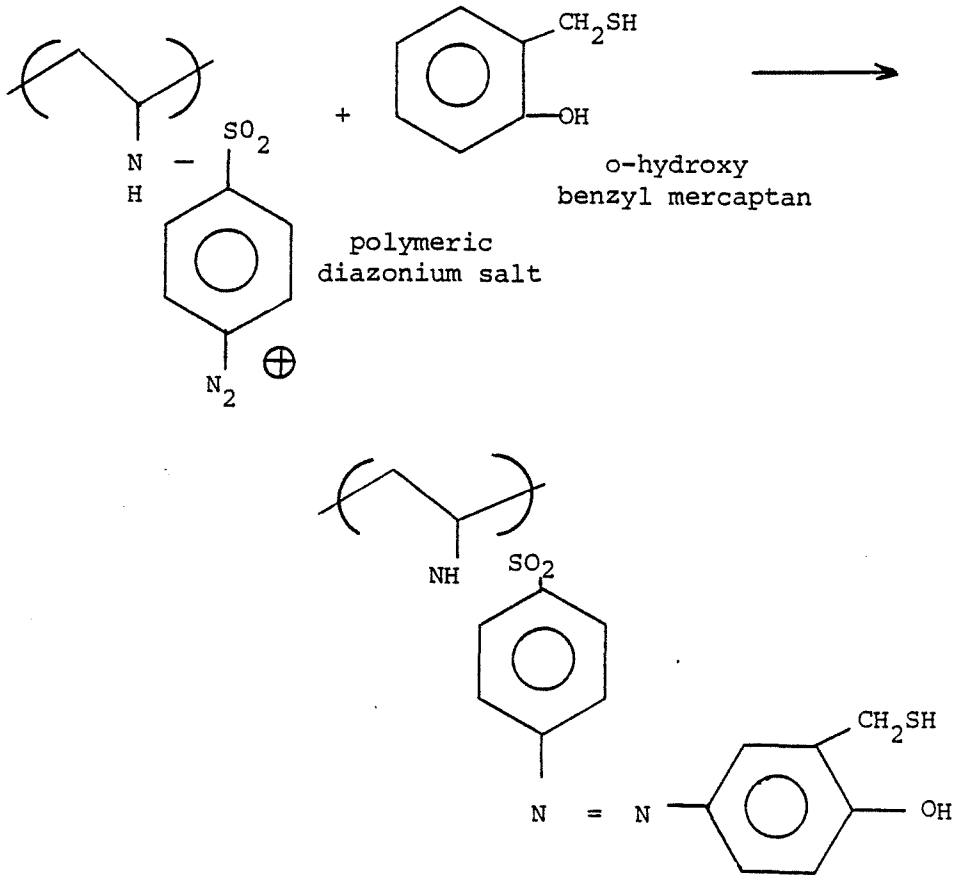
Azo linkages are thermally unstable and decompose on heating to release nitrogen gas. A stench agent linked to a polymer backbone through this type of structure would readily release the odorant on heating and the nitrogen evolved could serve to drive the odorant from the substrate. Such a coating could conceivably be made as follows:



amino functional polymer

acetanilide sulfonyl chloride

* AC = $\overset{O}{\overset{\|}{C}}-CH_3$



In this synthesis, the o-hydroxy benzyl mercaptan would serve as the odorant compound. For the Azo coupling reaction to take place, an aromatic compound is necessary. This limits the scope of potential odorant compounds, but it is likely that a compound of this type would be a suitable short-range stench agent.

All of these systems depend on the thermal decomposition of a covalent bond to release the stench agent. How readily this will occur may be determined from the relative bond strengths of the respective linkages. For comparison purposes, some representative values are listed below in Table 8.

TABLE 8

TYPICAL COVALENT BOND STRENGTHS

Bond	Bond Strength (Kcal/mole)	Coating System
C-O	257	Ester linked
C-N	184	Amide linked
Si-O	184	Siloxyl linked
C-S	175	Mercaptoester linked (Sulfide linked)
N-N	40	Azo linked

The most reliable thermal decomposition would occur with the Azo linked odorant. However, this type of system is probably the most difficult to prepare. In all cases, proper catalysis can lower the energy requirement for bond breakage between the odorant and the coating, enabling the stench agent to be released in the proper temperature range (150-200°C).

Another approach to a solvent-borne system is to use a polymeric coating with odorific thermal decomposition products. Most likely, these would be sulfur containing polymers such as polysulfides or thiourethanes. Coatings of this type are described in more detail below.

- Polysulfide Coatings

Mercaptan terminated polysulfide prepolymers are essentially high molecular weight mercaptans which contain ether and sulfide linkages. The manufacturer, Thiokol, believes that thermal decomposition products would have enough odor to function as an effective short-range warning.

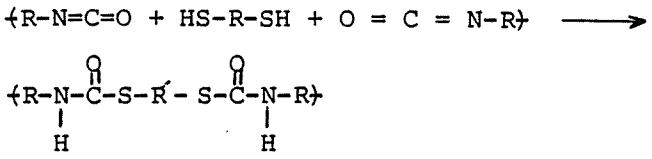
Polysulfide coatings can be applied from solution or as a 100% solids coating if the viscosity is sufficiently low. The coatings are generally cured with peroxide systems, and accelerators may be added to increase the cure rate. The cure reaction ties up the free mercapto groups, rendering the coating essentially free or odor. However, on heating the cure reaction may be reversible and odorific by-products should be formed. Because of this property, polysulfide coatings could be applied to mine timbers, cured, and then covered with a flame retardant coating such as an intumescent paint. When the timber is heated, thermal activation of the polysulfide would release odorant by-products from the coating.

A polysuflide/epoxy coating might work well as a topcoat when applied over impregnated timber.

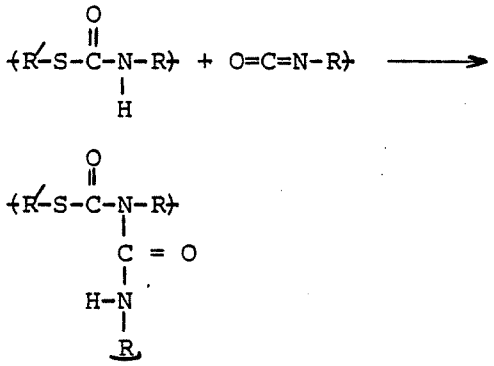
- Thiourethanes

Most polyurethane coatings are composed of polymers formed by the reaction of a diisocyanate with a diol or diamine. Because the cure reaction involves only the functional end groups of the reactants, many different coatings can be formulated with a wide variety of physical properties, depending on the molecular structure of the reactants.

Thiourethanes, or sulfur containing polyurethanes, can be made by reacting a diisocyanate with a dithiol. This reaction proceeds more slowly than the reaction between isocyanate and hydroxyl, but cure times can be increased by proper catalysis. A typical reaction of this type is shown below:



While the primary thiourethane linkage formed is not particularly thermally unstable, the reaction can proceed further in the presence of excess isocyanate to the allophanate stage:



This reaction forms allophanate crosslinks which may also contain dithiol units. These crosslinks are known to be thermally labile and would likely decompose on heating to release the thiol chain extender. The main chain thiourethane units may be sensitive to hydrolytic degradation, and may also decompose to some extent on prolonged heating in the presence of moisture. This reaction also could serve as a source of odorific by-products.

It appears that no prepackaged thiourethane systems are commercially available, but coatings of this type could be readily formulated from existing products. Hydroxyl terminated polyesters or polyethers can be reacted with diisocyanate to form prepolymers, or these materials can be purchased from various suppliers. The prepolymers can be chain extended with appropriate dithiols to produce the odorant coating desired. Coatings can also be formulated in one step (the "one shot" method) by combining the appropriate stoichiometric proportions of polyol, diisocyanate, and dithiol. It might also be worthwhile to consider the use of mercaptan terminated polysulfides in lieu of polyols in the preparation of thiourethane prepolymers and coatings. This would increase the potential odorant content of the coating and the likelihood of it functioning effectively in a stench warning application.

The only current commercial sulfur containing urethane is produced by American Cyanamid under the trade name Cytor. This product is a thermoplastic molding grade polyurethane based on conventional urethane chemistry. It is believed that sulfur is introduced into the polymer by using thiodiethanol as a chain extender.

Being a thermoplastic polyurethane, Cytor could be dissolved in solvent and applied to mine timber as an odorific coating, probably in conjunction with a sealant overcoating. Cytor is quite odorific at room temperature and Cyanamid has had difficulty establishing a market for the product for this reason. Due to lack of interest by the automotive industry, the market at which Cytor has been aimed, the product may be discontinued in the near future. However, it would not be difficult to formulate similar coatings, and this approach may be preferable, as odor properties could be custom tailored to a stench warning application.

- Polymeric Fixatives

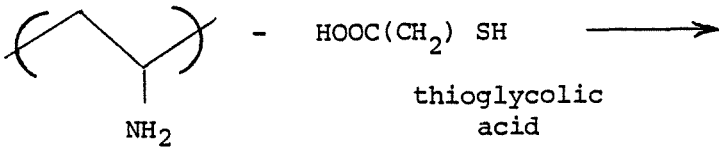
A different approach to solvent based stench warning coatings is to use a conventional coating as a fixative to retard release of monomeric stench agents at low temperatures. A coating solution could be mixed with a mercaptan and applied to mine timber. As the solvent evaporates, the mercaptan would remain dissolved within the coating material. It would be necessary to consider the competing relative evaporation rates of stench agent and solvent from the polymer, but careful selection of odorant and solvent could maximize both the amount of odorant retained and solvent lost. If the odorant is compatible with the polymer, it would remain within the coating and act much like a low molecular weight plasticizer. Heating such a system should result in increased odorant loss with increased mobility of the polymer chains surrounding the monomeric stench agent. A coating of this type would probably work best beneath an outer coating of intumescent paint.

Water Borne Coatings

Modified water based coating systems also offer potential as stench warning materials. Generally, aqueous coatings can be divided into two types: aqueous solutions and latexes. Several water-based systems offer potential for ionically binding selected odorants to the polymer chains, thereby increasing the permanence of the stench agents. This can be done most easily with amino functional polymers, by taking advantage of either the acidity of the mercapto hydrogen or some other functional group contained in an odorant compound and the basicity of the amino group. Reaction between the two produces a salt and the odorant compound becomes ionically bound to the polymer. Dissociation of the stench agent from the polymer would likely occur at a more rapid rate with increased temperature.

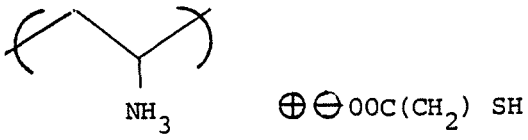
- Aqueous Solutions

Aqueous solutions of poly(ethylenimine) and poly(vinyl amine) can be reacted with acidic odorant compounds like thioglycolic acid, a water soluble mercaptan. This reaction is shown below:



thioglycolic acid

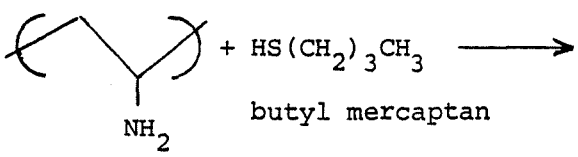
poly(ethylenimine) or
poly(vinyl amine)



polymer-odorant salt

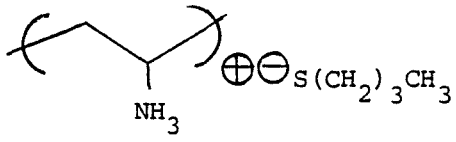
To ensure that the odorant compound reacts completely with the polymer, a stoichiometric deficiency of odorant should be used (e.g. 0.9:1.0).

It may be possible to react a mercapto group with an amino functional polymer as well, considering the mildly acidic nature of the mercapto hydrogen.



butyl mercaptan

poly(ethylenimine) or
poly(vinyl amine)



polymer-mercaptan salt

Although butyl mercaptan is only slightly water soluble, the reaction should take place if sufficient agitation is present.

The applicability of stench warning systems of this type will depend on the degree to which thermal dissociation of the salt will occur. Availability of the polymer solutions also must be considered; poly(vinyl amine) is not commercially available in the U.S., although it is manufactured and used in-house by Dynapol of Palo Alto, CA as a polymeric dye intermediate. Poly (ethylenimine) is produced by Cordova Chemical Co. of Sacramento, CA, but other companies like Dow Chemical have discontinued manufacture of the polymer due to concern over possible carcinogenic activity of the monomer.

The problem of polymer availability can be circumvented by modifying more readily available water soluble resins to incorporate ionic functional sites onto the polymer. Some possible methods of doing so are outlined in Table 9, followed by several examples. The table gives functionality requirements for the polymer, the "bridge" compound, and the odorant compound. The bond between polymer and bridge compound will be covalent, while the bridge-odorant bond will be ionic.

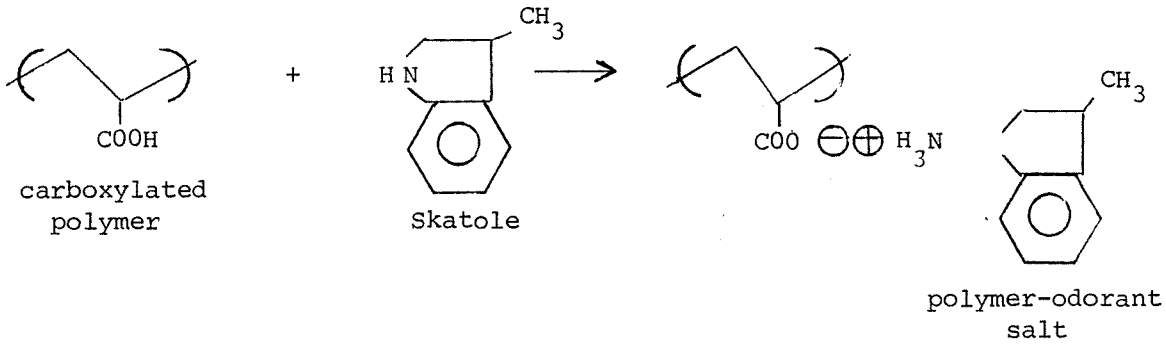
TABLE 9

FUNCTIONALITY REQUIREMENTS FOR THE INTRODUCTION OF IONIC SITES INTO WATER SOLUBLE POLYMERS

Polymer Functionality	Bridge Compound Functionality (Difunctional)		Odorant Functionality
	None		
Carboxyl	Hydroxyl	Amino	Amino
Carboxyl	Carboxyl	Amino	Carboxyl
Hydroxyl	Carboxyl	Carboxyl	Carboxyl
Hydroxyl	(Anhydride)		Amino

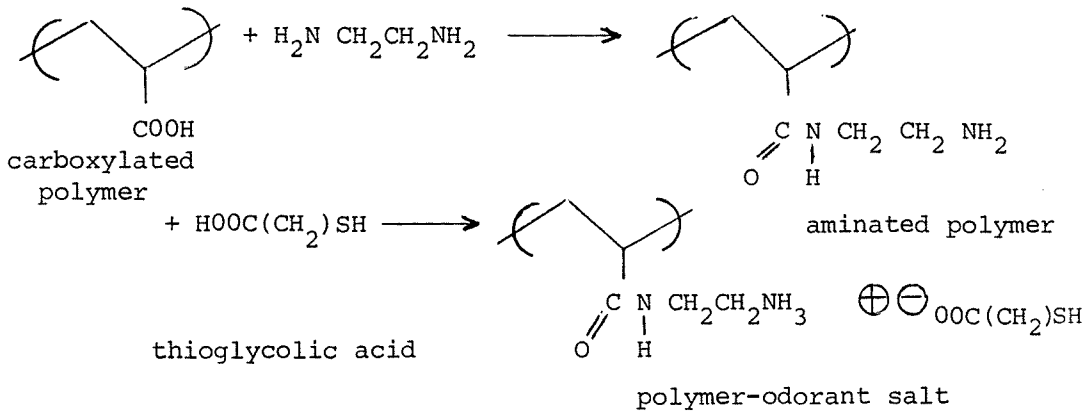
- Reaction of a Carboxyl Functional Polymer with an Amino Functional Odorant (No Bridge Compound Required)

A carboxyl functional polymer such as carboxymethyl cellulose or a water soluble carboxylated acrylic could be reacted directly with an amino functional odorant to form an ionic bond:



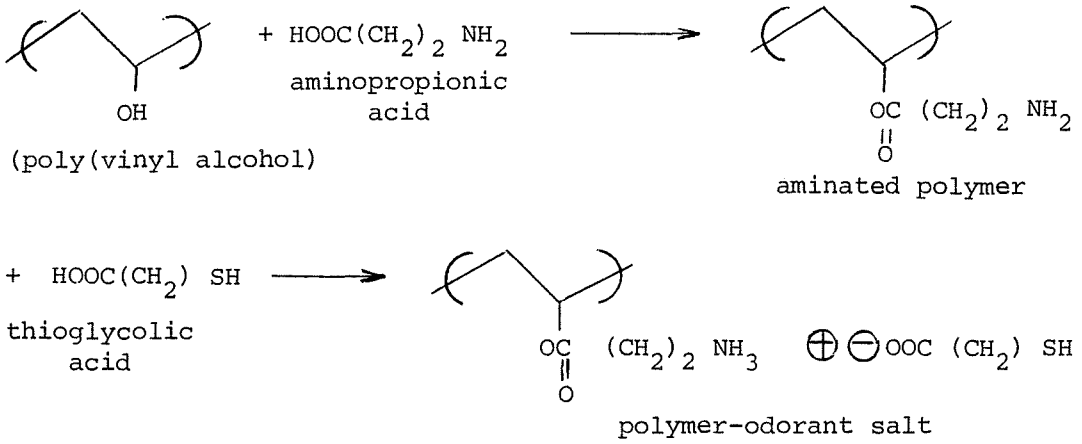
- Use a Diamino Functional Bridge Between a Carboxyl Functional Polymer and a Carboxyl Functional Odorant

Compounds like ethylene diamine could be used to provide bridges between carboxylated polymers and carboxyl functional odorants:



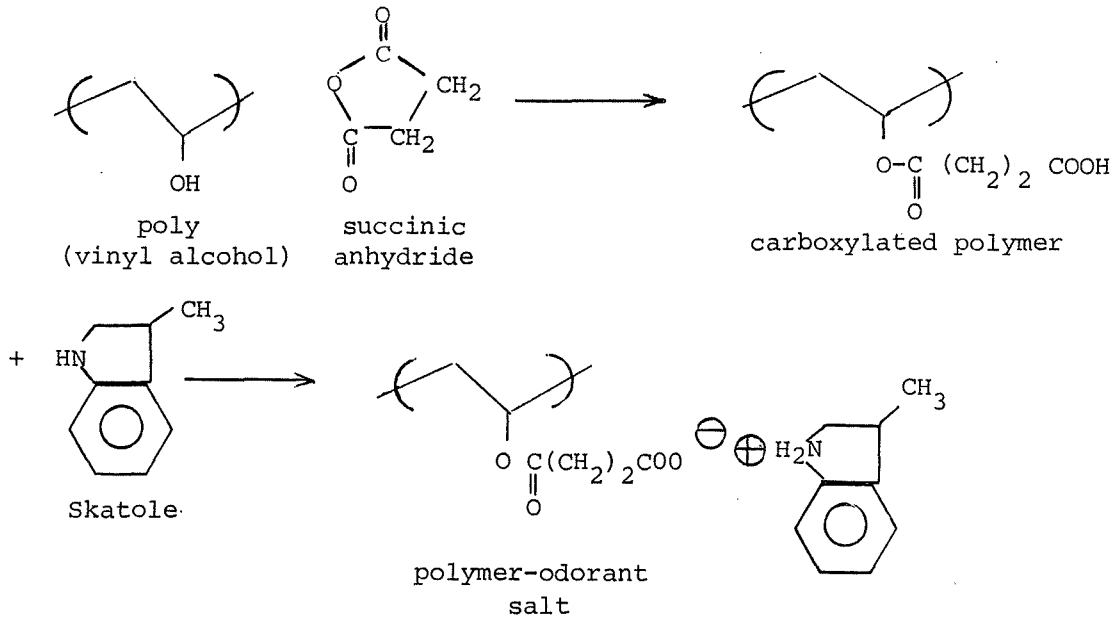
- Use of Carboxyl/Amino Functional Bridge Between a Hydroxyl Functional Polymer and a Carboxyl Functional Odorant

A poly(vinyl alcohol) resin could be reacted with an amino acid to introduce amino functionality into the polymer:



- Use of an Anhydride Bridge Between a Hydroxyl Functional Polymer and an Amino Functional Odorant

An anhydride could be used to link an amino functional odorant to a hydroxyl functional polymer:



- Latexes

Vinyl pyridine latexes are available from several major rubber companies including B. F. Goodrich and General Tire. A vinyl pyridine polymer contains basic sites which can be used to form salts with acidic odorants, providing the odorant did not cause coagulation of the latex. If this was a problem, the coating could be applied to the wood as a latex and the odorant could be applied and reacted to the coating surface. The bound odorant could then be covered with an outer layer of a barrier coating.

- Water Soluble Polymeric Fixatives

As previously described, coatings can be used as fixatives to retard loss of odorant compounds that are not chemically reacted to the coating. It would be desirable to use water soluble polymers to fix water soluble odorants like skatole; the two would likely be more compatible and the fixative would be more effective in retaining the odorant. Using this approach, aqueous solutions of vinyl alcohol or vinyl pyrrolidone resins might serve as suitable fixatives for heterocyclic nitrogen compounds like indole and skatole.

Timber Impregnation

Stench warning systems using timber impregnation techniques have only briefly been investigated as alternatives to coatings. Impregnated stench agents might prove to be more permanent since the odorant is required to diffuse from the interior to the surface of the treated wood, but this could also hinder the release of odorant when thermally activated. It would take a longer time for stench agent within a mine timber to sense heat from an external source, delaying the release of odorant to the environment. Also, impregnation of impermeable woods such as Douglas fir with non-aqueous solutions has proven very difficult, and the majority of odorants considered useful are not water soluble.

For the sake of completeness, several impregnation approaches are considered as alternatives to coating techniques.

- Aqueous Impregnation

An aqueous solution of water soluble odorant, odorant fixed with water soluble polymer, or odorant reacted to a water soluble polymer, could be pressure impregnated into mine timber. After such treatment, an outer coating would probably be required to help seal in the stench agent and to afford desired flame retardancy. Candidate materials for this type of treatment would be vinyl alcohol and vinyl pyrrolidone resins, and odorants like skatole and indole.

- Non-Aqueous Impregnation

Thiokol has suggested attempting to impregnate polysulfide resins into mine timber. If uncured resin could be impregnated, curative could be brushed onto the surface of the wood, allowing the outer surface to cure, locking the

uncured polysulfide into the wood to serve as an odorant. Attempts could be made to impregnate other sulfur containing polymers or polymer/odorant systems into mine timber as well, but the difficulties associated with impregnation using a high viscosity, non-aqueous system may prove difficult to overcome.

Non-Coating Techniques

The stench warning concept development to this point has been directed primarily at coatings which would act as odorant compounds or serve to contain stench agents by chemical or physical means. However, a separate coating may not be necessary if an odorant can be held in place on the surface of a mine timber.

Because wood is primarily cellulosic in nature, the exposed surface of a mine timber can act much like a hydroxyl functional polymeric coating. All of the methods that have been previously considered regarding the chemical attachment of odorants to hydroxyl functional polymers should apply to wood as well. This would include the chemical reaction with mercaptosilanes, formation of esters with carboxyl functional odorants, and the use of bridge compounds to provide basic sites on the wood surface for salt formation with acidic odorants.

If an odorant could be successfully reacted with the cellulosic hydroxyl groups, the need for a coating as part of the system could be eliminated permitting quicker and less expensive application of the odorant. Using this approach, a top coat of flame retardant paint would probably be required to retard loss of any unreacted or dissociated stench agent.

It may also be possible to apply odorant to mine timber in patches, probably as admixtures with a monomeric fixative. A variety of odorant compounds including sulfur organics, fragrances, musks, or nitrogen heterocycles, could be admixed with mineral oils, glycols, polyols, or even low melting solids like waxes or polycaprolactones to produce fixed odorants for direct application to the wood. Odorant could be applied to portions of selected timbers, especially where exposure to potential fires is likely, such as a timber side facing electrical equipment. This type of application would also require some type of external coatings to help retain the odorant compound. Normal flame retardant might be adequate for this purpose.

Physical Containment Techniques

All treatment concepts considered thus far have relied on odorant containment by the wood (impregnation) or some type of coating applied as an integral part of the mine timber. Odorant compounds could also be effectively sealed in capsule-like units designed to release the stench agent at a predetermined temperature. Such devices would be similar to the so-called "stench capsule" developed by the British Safety in Mines Research Establishment. The SMRE stench capsule was a metal container with a fusible plug, designed to melt and release odorant when exposed to heat. Similar devices could be fabricated to produce odorant packages that could be physically attached to mine timbers near potential

sources of ignition. Plastic materials and packaging technology could be used to economically produce this type of stench warning system. Several methods of producing these units are described below.

- Plastic Tube/Pouch (Figure 9)

A continuous tube of packaging film, probably low density polyethylene or ethylene-vinyl acetate copolymer could be simultaneously filled with odorant, heat sealed, and cut into individual pouches. Holes could be punched into the sealed areas of the pouches in the same operation to facilitate fastening to the timber. Pouch size would be determined by the amount of odorant required, probably not more than 10 to 20 ml, depending on the odor characteristics of the stench agent.

This type of stench warning device would offer very tight control over both evaporative losses (should be minimal) and activation temperature of the system. By proper selection of materials, barrier properties of the pouch can be maximized to suit the odorant used, and the melting point of the pouch material will determine the activation temperature of the device.

A wide variety of plastics could be used as the pouch material. If heat sealability of a particular material is difficult, it could be coated with a hot melt adhesive layer, side-seamed to form a tube, then filled and heat sealed.

Although a system of this type would be inexpensive and simple to put into operation, pouches of this type might rupture during handling if the film is not sufficiently thick. Also, exposed pouches could be a target for vandalism. Flammability of the packaging material should be considered, but the small size of the containers would probably minimize this concern.

- Foil Tube/Pouch

For better barrier properties, metal foils could be coated with hot melt resins and side seamed to form a tube. As with the plastic pouch concept, such a tube could be filled with odorant and sealed to produce foil pouches. A dark outer coating would serve to absorb radiant heat in the event of a fire.

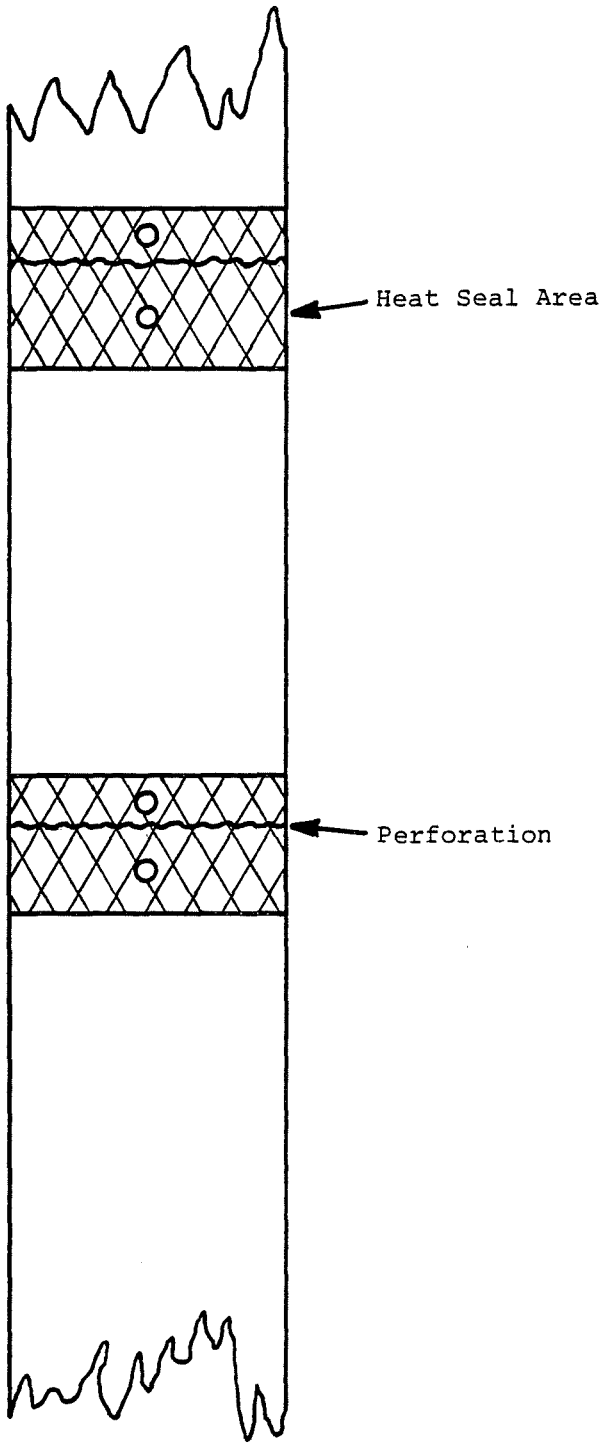
The foil pouch offers impermeability that cannot be matched by a plastic pouch. If permeation of plastic pouches by odorant compounds is a problem, foil pouches would be preferable. This type of pouch would also be more durable than one of all plastic construction, and the foil exterior would not be flammable.

- Hollow Stud

A hollow stud with a pointed tip could be filled with odorant, sealed, and driven into a mine timber. The concept is essentially identical to the SMRE stench capsule, but the construction is simpler and the fusible plug employed would probably be plastic or wax. The major advantage of the stud design is that the unit is concealed within the timber with only the plug exposed to the

FIGURE 9

CONCEPT FOR STENCH WARNING DEVICE -
PLASTIC TUBE OR FOIL POUCH



surface. This type of design would make the unit more tamper-proof than an exposed pouch, and the simplicity of the design should make the stud less expensive than the SMRE stench capsule. In addition, the nearly all-metal construction would make the unit non-flammable.

The design requires that a filled and sealed unit be driven into the timber like a nail; this might have to be done carefully so as not to loosen the fusible plug. Another disadvantage is that more heat would probably be needed to activate a system of this type compared to an exposed stench pouch. The metal body of the unit would probably make the capsule more expensive than a stench pouch.

- Hollow Capsule Insert (Figures 10 and 11)

Based on the hollow stud concept, a hollow plastic capsule could be injection molded, filled with odorant, and sealed, (Figure 10). A flanged surface would permit the opening to be sealed with a dark colored plastic film or hot melt coated metal foil.

Construction of this type offers advantages similar to the hollow stud, and the cost would probably be less. This type of capsule would be more expensive to produce than the pouch type capsule, but the unit would be considerably more sturdy and less prone to accidental rupture during handling and installation. Of the systems considered to this point, the hollow capsule insert would require the most time to install, since it would be necessary to drill a hole in the timber to accept the capsule.

Hollow capsule inserts could also be made by a thermoforming process from plastic sheet stock (Figure 11). This is a less expensive alternative to injection molding since many capsules could be formed from a single sheet. After forming, the capsules could be filled with odorant and sealed using a hot melt coated cover film or foil. The result would be a formed, filled, and sealed sheet of many stench capsules. These sheets could then be transferred to a die where the individual capsules would either be cut apart, or perforated for later separation from each other. The finished capsule would resemble the small coffee creamer containers currently used by many restaurants. Probable materials of construction would be high density polyethylene or polypropylene for the body of the insert, and hot melt coated high density polyethylene film or foil for the cover seal.

Conclusions

The present concept development has divided short-range stench warning systems into two types: those applied directly to mine timbers which become part of the timber and systems which are physically separate from the timber. In the first category are coatings, odorants used with fixatives, and odorants reacted to the timber itself. The second classification covers physically contained stench packages which are later attached to the wood. The systems envisioned have identified the following as viable approaches to developing an effective short range mine stench warning system:

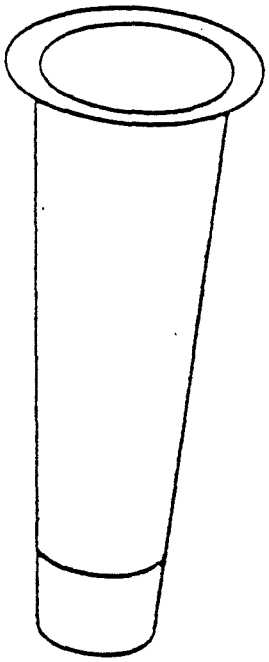


FIGURE 10

INJECTION MOLDED PLASTIC TUBE

Thermoformed Sheet Using Multi-Cavity Mold

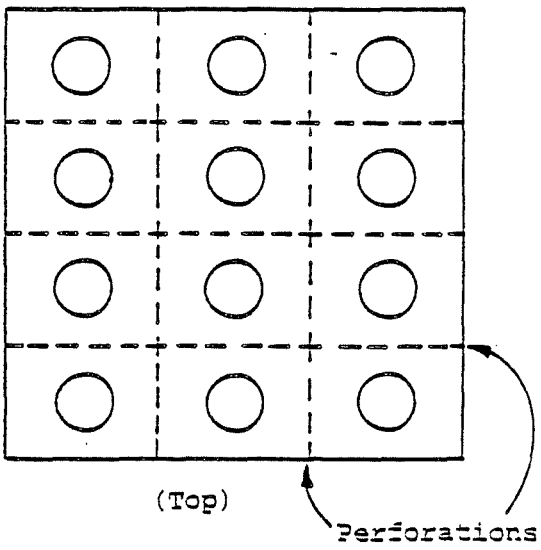
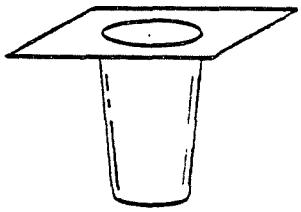


FIGURE 11

THERMOFORMED PLASTIC TUBE

Single Thermoformed Capsule



1. Functional mercaptans can be chemically bound to selected polymer coatings. Siloxyl, sulfide, ester, mercaptoester, amide, and azo linkages between odorant and coating may be thermally decomposed to release the stench agent. A conventional timber coating would probably be desirable as a topcoat.

2. Polymers containing basic groups can be reacted with acidic stench agents to produce salts which may decompose on heating to liberate the odorant. If availability is a problem, common resins like poly(vinyl alcohol) can be modified to "build in" basic functionality for polymer odorant salt formation.

3. Polysulfides and thiourethanes may function as polymeric odorants which would decompose on heating. Coatings of this type would likely be used with a conventional topcoat.

4. Water or solvent borne polymers might serve as fixatives for various stench agents, to retard odorant loss without being chemically bound to the polymer. Materials of lower molecular weight like oils, glycols, or waxes might also serve this purpose.

5. Odorant or odorant/fixative admixtures can be impregnated into mine timber, but this may prove difficult, especially with non-aqueous solutions.

6. The hydroxyl functionality of wood can be used to directly react odorant to the mine timber. This system does not require a fixative coating, although flame retardant topcoat would be recommended.

7. Various physical containment techniques enable odorant to be released at elevated temperatures. These devices would be separate from the timber itself, and would probably be in the form of plastic or foil pouches attached to the timber, or hollow studs or capsules inserted into the timber.

7. CONDUCT A PRELIMINARY EVALUATION OF STENCH WARNING MATERIALS FOR USE ON WOOD MINE TIMBERS

Based on the concepts developed in Section 6 (page 48), a preliminary evaluation of stench warning materials was conducted. To avoid possible duplication of effort, these investigations excluded the physical containment methods such as stench warning capsule with fusible plug, and focused on the remaining concepts.

The "non-containment" concepts can be categorized as either wood coupling treatments, wood impregnants or coatings. In order for a heating system to be most effective, the agent must sense the heat from the "heating" or fire as quickly as possible. Impregnants and wood treatments will depend on the mass of the wood heating up to the release temperature of the agent before stench warning is released; such systems will probably be slow and possibly damaging to the timber.

Therefore, our preliminary investigation of stench warning materials was limited to continuous coatings and coating-like patches which could be applied on top of or directly under the intumescent fire retardant coating.

The following concepts were given a preliminary evaluation:

- Polysulfide Coatings: These coatings were prepared from commercially available crosslinkable prepolymers. Since the stench "agent" in the form of terminal ethyl mercaptan groups is chemically bound to the polymer, there would be no concern with low level odor or evaporative losses in the unactivated state.

- Basic Polymer/Acidic Agent Salts and Acidic Polymer/Basic Agent Salts: Using polymeric materials such as polyethylenimine which is a film former if applied from water solution, we prepared salts with stench agents such as thioglycolic acid. The ionic bond reduces the volatility of the agent and minimizes evaporative losses, but permits release of the agent on heating.

- Oil Soluble Polymeric Fixatives: Candidate stench warning agents were dissolved in polymeric binders which were chemically similar and largely amorphous (non-crystalline). It was presumed that if the compatability between agent and polymer were good, the partial pressure of the agent (at 1 to 5% in the resin) would be extremely low and evaporative losses in the unactivated state would be insignificant.

- Odorant Chemically Bonded to a Polymer: Once again, the chemical bonding should eliminate evaporative losses in the unactivated state. These systems were given lower priority in our preliminary screening because they involved more effort to prepare and demonstrate.

Thin films were prepared from mixtures of coating resins and stench agents where appropriate. These films were evaluated qualitatively by heating small samples on a hot bench at approximately 220°C. Promising films which had little or no odor at ambient conditions but which gave a strong odor on heating were also evaluated by Thermogravimetric Analysis (TGA). The TGA analysis provided an indication of release rate in the form of weight loss versus temperature.

Polysulfide Coatings: Based on supplier recommendations, a polysulfide rubber compound was formulated based on liquid polysulfide prepolymer as follows:

Material	Grade	Manufacturer	Parts by Weight
Polysulfide	LP-31	Thiokol Chemical	100
Calcium Carbonate	Hi Flex 100	Pfizer	50
Lead Peroxide	FC	Eagle Pitcher Industries	5
Stearic Acid	Practical	Matheson Coleman and Bell	0.1
Alumina	Alon C	Cabot Corp.	0.2

The compound was mixed by hand, poured into an aluminum pan sprayed with fluorocarbon release agent, and cured for two hours at 70°C. The resulting sheet of rubber had reasonably good strength and elongation and should be sufficiently durable as a coating or patch.

TGA analysis indicated that the polysulfide lost 2.1% of its weight by 200°C and 7.6% of its weight by 250°C, but qualitative evaluation at 220°C yielded only a faint and rather indistinct odor. The odor was musky rather than pungent as normally associated with low molecular weight mercaptans. No further work was done with the unmodified polysulfide.

Basic Polymer/Acidic Agent Salts and Acidic Polymer/Basic Agent Salts: All candidate "polymeric salts" were prepared by solution blending using commercially available materials. Water solutions of polymers such as polyethylenimine and Carboset acrylic/acid multipolymer were combined with methanol solutions of the appropriate agent. Films cast from solution were evaluated for odor release by heating on a hot bench at 220°C.

The basic polymer/acidic agent material is represented by the polyethylenimine/thioglycolic acid salt (A-14190-A) in Table 10. The materials were combined at a ratio of 1 mole of acid per two moles of amine in order to avoid having excess volatile thioglycolic acid.

The dry polymer film exhibited only a faint to moderate sulfur-like odor at ambient conditions, but released a strong sulfur odor when heated at 220°C.

Three acidic polymer/basic agent salts were prepared based around Carboset 525, an acid containing water soluble acrylic resin. Salts were formed by combining the Carboset with one of three amine containing stench compounds, indole, skatole (3-methyl indole), and methyl anthranilate (see Table 10).

TABLE 10

ODOR RELEASING CHARACTERISTICS OF
WATER-BORNE POLYMER/ODORANT SALTS

						Odor	
Sample Number	Polymer (Manufacturer)	Resin Type	Stench Agent	phr	Solvent System	At Room Temperature	at ~220°C
A-14190-A	Corcat P-600 (Cordova Chemical)	polyethylen-imine	thioglycolic acid	107	water	faint to moderate	strong sulfur odor
A-14191-A	Carboset 525 (B. F. Goodrich)	acid containing acrylic polymer	skatole (3-methyl indole)	3.6	water/ methanol	faint to moderate	moderate to strong
A-14183-A	Carboset 525	acid containing acrylic polymer	methyl anthranilate	16.6	water/ methanol	strong	---
A-14189-A				12.4		faint	moderate to strong
A-14183-B				4.2		very faint	moderate to strong
A-14189-B	Carboset 525	acid containing acrylic polymer	none (control)		water/ methanol	---	---
A-14183-D	Carboset 525	acid containing acrylic polymer	indole	6.4	water/ methanol	faint to moderate	strong

Skatole was combined with Carboset at 0.25 moles of amine per mole of acid in order to avoid having an excess of volatile skatole in the final polymer. A cast film gave a faint to moderate odor of skatole at ambient conditions, but a moderate to strong odor when heated at 220°C.

Films prepared with 0.8 moles of methyl anthranilate per mole of acid (A-14183-A) had a strong odor of violets at room temperature while films prepared with only 0.2 and 0.4 moles of methyl anthranilate had only faint odors (A-14183-B and A-14189-A). The latter two films when heated at 220°C gave moderate to strong odors.

An indole/Carboset salt was prepared at a ratio of 0.4 moles amine to one of acid (A-14183-D); again the odor at 220°C was strong.

Both indole, and particularly skatole (3 methyl indole) give strong putrid odors while methyl anthranilate gives a rather pleasant odor of violets. From the standpoint of stench warning, the two indole based materials would probably be preferred.

Oil Soluble Polymeric Fixative Coating: Candidate systems for this concept appear in Table 11. Samples were prepared by blending solvent solutions of stench warning agent with solutions of chemically similar polymeric film formers. Stench agents were screened at 1 to 5 phr (parts by weight of agent per hundred parts of polymer).

In general, both vanillin and menthol gave too delicate and indistinct an odor to be effective as a warning agent. In particular, the menthol seems to be felt rather than really smelled, and is not pungent as in the case of the mercaptans and indoles.

For the most part, the concept does not seem to minimize the room temperature odor of the agent/polymer film as well as the polymer odorant salts in which the agent is more tightly held.

With the exception of skatole in Elvamide 8063, none of the formulations gave a particularly strong odor when heated at 220°C. To have added more than 1 phr agent to most of these formulations would only have increased the odor at ambient conditions.

Sample A-14178-B which comprised 2 phr thioglycolic acid in a polysulfide rubber formulation similar to that on page 70, would not cure even when heated overnight at 60°C. Substituting dodecylmercaptan for the thioglycolic acid (A-14192-B) eliminated this problem.

Odorant Chemically Bonded to a Polymer: The system investigated in this category is the reaction product of a mercaptan and glycidyl methacrylate copolymer. Since we knew of no commercially available copolymers of this type, the first step was to prepare a copolymer by solution polymerization.

The following methyl methacrylate (MMA), butyl acrylate (BA), glycidyl methacrylate (GMA) terpolymers were prepared using lauroyl peroxide (L_2O_2) as the free radical initiator.

TABLE 11

ODOR RELEASING CHARACTERISTICS OF
OIL SOLUBLE POLYMER FIXATIVES

Sample Number	Polymer (Manufacturer)	Resin Type	Stench Agent	phr	Solvent System	Odor		TGA Weight Loss %/T°C
						At Room Temperature	At ~220°C	
A-14180-B-1	Elvamide 8063 (DuPont)	polyamide	Skatole	1.0	Toluene/ acetone	moderate to strong	moderate to strong	---
A-14180-C-3	Vitel PE-222 (Goodyear)	polyester	Methyl Anthranilate	1.0	Toluene/ methyl ethyl ketone	faint	faint to moderate	---
A-14180-D-1	E-398-10 (Eastman)	cellulose acetate	Vanillin	1.0	acetone	faint to moderate	faint to(1) moderate	---
A-14180-F-1	Macromelt 6900 (Henkel)	polyamide	Indole	1.0	methylene chloride/ methanol	faint	faint	
A-14185-G-1	E-398-10 (Eastman)	cellulose acetate	Menthol	1.0	acetone	none	faint -(1) burnt sugar odor	
A-14185-G-2	E-398-10	cellulose acetate	Menthol	5.0	acetone			
A-14180-H-1	Macromelt 6900	polyamide	Menthol	1.0	methylene chloride/ menthol	faint to moderate	faint - (1) burnt sugar odor	0.66% @ 250°C
A-14180-A-1	Macromelt 6900	polyamide	Methyl Anthranilate	1.0	methylene chloride/ menthol	faint to moderate	faint to moderate	negligible
A-14178-B	LP-31 (Thiokol)	polysulfide	Thioglycolic acid	2.0	none	(2)	(2)	
A-14192-B	LP-31 (Thiokol)	polysulfide	dodecyl mercaptan	2.0	none	faint	faint	

(1) may be too delicate and indistinct an odor

(2) rubber would not cure

Material	Weight in Grams				
	A-14181-			A-14182-	
	A	B	C	A	B
MMA	22.5	22.5	22.5	22.5	37.5
BA	6.0	3.0	6.0	6.0	10.0
GMA	1.5	1.5	1.5	1.5	2.5
Ethyl Acetate	---	---	35.0	35.0	25.0
Toluene	70.0	70.0	35.0	---	---
Cyclohexane	---	---	---	35.0	25.0
Alperox F (L_2O_2)	0.15	0.15	0.15	0.30	0.50
Temperature (^oC)	60			70	

The reactants were charged into 7 ounce pop-bottles, flushed with high purity nitrogen, capped and tumbled in a controlled temperature diethylene glycol bath for 20 hours. Percent conversion was determined gravimetrically on weighed and dried samples of solution.

The A-14181 series was low in percent conversion of monomer to polymer; conversions were 71, 69 and 67 percent respectively. In an effort to raise the conversion in series A-14182, we:

- Increased the initiator concentration from 0.5 to 1.0 phr,
- Substituted cyclohexane for toluene to reduce chain transfer to solvent,
- Increased the temperature 10 degrees centigrade to increase the rate of reaction, and increase the decomposition rate of free radical initiator, and
- On sample A-14182-B, decreased the proportion of solvent, again to minimize chain transfer to solvent.

The percent conversion on this series of polymerizations were 90 and 96 percent respectively; sample A-14182-B was judged suitable for reacting with mercaptan.

The GMA copolymer was reacted with dodecyl mercaptan as follows:

Material	Type	Manufacturer	Parts by Weight
A-14182-B	GMA copolymer	--	50 solution (14.25 resin)
Dodecyl mercaptan	---	Pennwalt	0.855
DMP-30	2,4,6 tri (dimethyl-aminomethyl) phenol	Rohm & Haas	0.15
DABCO	triethylene diamine	Air Products	0.01

The proportions represent 0.8 moles of mercaptan per mole of glycidyl methacrylate; again this was done to avoid an excess of the volatile mercaptan.

A masterbatch of catalyst (DABCO) and accelerator (DMP-30) was prepared in dodecyl mercaptan; the mixture was heated at 60°C to dissolve the DABCO. The masterbatch was then added to the resin solution which was heated for four hours at 60°C.

The mixture was cast into a film and dried at ambient conditions. The resulting film had a moderate odor at ambient conditions and gave off a strong "burnt rubber" odor when heated at 220°C. The odor, although strong, was not distinctive and would probably not be desirable for a warning agent.

This concept bears further investigation using lower molecular weight and more pungent mercaptans.

Preliminary Conclusions: Of the stench warning materials evaluated, those chemically bound to the polymeric coating either through direct chemical reaction or through salt formation appear to be most promising. The odor at ambient conditions is generally faint while the odor in the release range (220°C) is for the most part moderate to strong.

On the other hand, the oil soluble fixative coatings are not particularly promising. Dissolving of the stench agent in a high molecular weight amorphous polymer of similar composition is not sufficient to prevent significant loss of odorant at ambient conditions and therefore the odor at ambient temperatures approaches that at the release temperature of 220°C.

Additional work is required on the water soluble polymer/odorant salts to verify the effectiveness of the concept in simulated end use conditions, and to overcome problems of water sensitivity with such salts.

One method of reducing water solubility might be to overcoat the stench agent coating or patch with a barrier coating of some high molecular weight hydrophobic polymer.

Solutions of both indole and skatole tend to discolor on standing which suggests that the amine groups may be oxidizing; this should be verified before any further work is done with these materials. This problem was not evident with methyl anthranilate.

Further work should also be done to document the lack of toxicity for any of the candidate odorants to be examined.

8. CONCLUSIONS AND RECOMMENDATIONS

On the basis of small scale tests, the optimum treatment system, 3.5 pounds/ft^3 of Fyreprufe and 1.0 pounds/ft^3 of Acid Copper Chromate (ACC) overcoated with 3.5 mils of Albi 107A and 1.0 mils of Albi 144, gave very promising results when applied to Ponderosa pine samples. Flame spread rating by two foot tunnel was 26.7 $\pm$ 2.7 and weight loss in the E-69 fire tube was only 10.7% $\pm$ 0.6%. Earlier investigations at 6.0 pounds/ft^3 Fyreprufe and 7.0 mils Albi 107A indicated that treated pine samples when tested in the NBS smoke density chamber gave D_m (maximum specific optical densities) of 184 and 152, flaming and smoldering respectively[2]. These values were well below the acceptable limit of 300.

Prior investigations on treated pine also showed acceptable levels of toxic gases such as carbon monoxide, HCN, SO_2, HCl, Cl_2, ammonia, phosgene and aldehydes in both the smoldering and flaming modes in the NBS smoke density chamber when tested at 2.5 watts/cm^2 [2].

There was evidence of reduced compressive strength in Fyreprufe treated pine even at retentions as low as 3.5 pounds/ft^3. Of course, this data was obtained in a species not generally used for structural timber. For roof support timber such as Douglas fir, the depth of penetration during impregnation is seldom greater than 0.5 inches. Therefore, the main body of a structural 12" x 12" or 10" by 10" timber would be uneffected.

During the current effort, annualized manufacturing costs were developed for both the Fyreprufe/ACC impregnation and Albi 107A/144 coating portions of the treatment based on model processes. The annualized costs of manufacture (not selling price) for the treatment portion of the process exclusive of the cut and framed timber are estimated to be:

Impregnation with Fyreprufe/ACC:	\$ 63.00/K bd. ft.
Coating with Albi 107A/144:	\$ 112.00/k bd. ft. or
	\$ 0.33/ft^2

These costs compare favorably with the current selling price for untreated cut and framed 12 x 12" timber of between \$400 and \$600/K bd. ft. depending on the type of wood, quality of the grain, and degree of cutting and framing required.

Therefore, we recommend that further larger scale testing be conducted based on the Fyreprufe/ACC Albi 107A/144 system. Such evaluations might include ASTM E-84, "Test for Surface Burning Characteristics of Building Materials" or medium or large scale simulated mine tunnel fire tests.

The wood timber of choice for such testing is Douglas fir, a material commonly used for structural timber in underground metal and non-metal mines.

Several stench warning materials were evaluated for use as localized heat warning materials for wood mine timber. Of those tested, polymer/odorant salts showed the most immediate promise. Additional work is required, however, to develop a viable warning system. Additional testing must be conducted in simulated end-use conditions, and methods or materials must be identified to reduce the water sensitivity of the polymer/odorant salts.

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APPENDIX

Cost Factors for Task 2: Develop a Model Manufacturing Process for Timber Treatment and Estimate Associated Annualized Costs

Materials

Impregnation Salts: The material requirement assumes the impregnation of 12" x 12" timbers to a depth of 0.4 inches at a retention in the impregnated portion of the timber of 3.5 pounds per cubic foot of Fyreprufe and 1.0 pounds per cubic foot of acid copper chromate.

The annual consumptions are calculated to be as follows:

Material	Rate (lbs/1000 bd. ft.)	Annual Total; Pounds (for 3000 K bd. ft./yr.)
Fyreprufe	46.2	138,600
Acid Copper Chromate	13.2	39,600

Allowing 5% for material losses in handling the salt costs are determined to be:

Annual Fyreprufe Cost

Ingredient	Weight %	Price/Pound, $[(1)]	Total Cost, $
Ammonium Sulfate	89	0.0325	4,210
Diammonium Phosphate	5	0.475	3,460
Sodium Dichromate	2	0.55	1,600
Sodium Fluoride	4	0.364	2,120
		TOTAL COST	11,390

Annual Acid Copper Chromate Cost

Sodium Dichromate	48.3	0.45	9,040
Copper Sulfate	50.0	0.4545	9,450
Chromium Trioxide	1.7	1.24	880
		TOTAL COST	19,370

Coating Materials: The coating material costs assume coating 3000 K bd. ft. of 12" x 12" timber or 1,070,000 ft^2/year assuming a 90% paint utilization. The costs are as follows:

Paint	Coverage ft^2/gallon	Total Gallons	Price/Gallon, $	Total $
Albi 107A	300	3,970	23.55	93,500
Albi 144	450	2,660	22.35	59,450

(1) Salt prices based on "Oil Paint and Drug/Chemical Marketing Reporter" - fourth quarter 1981.

Paint prices are based on verbal quotes from Albi, Division of Stanchem, Berlin, CT.

For flow coating of the intumescent paints, we have assumed a volume dilution of 1.5 parts of solvent per part of paint, based on xylene for thinning of the Albi 107A and mineral spirits for Albi 144.

Solvent	Total Gallons	Price/Gallon:$	Total Cost: $
Xylene	5,955	1.50	8,932.50
Mineral Spirits	3,990	1.41	5,625.90

Solvent prices are based on "Oil Paint and Drug/Chemical Marketing Reporter".

Capital Equipment

Written quotations were obtained on the following equipment:

Equipment	Vendor	Location	Price: $
Corley Incisor	Corley Manufacturing Company	Chattanooga, Tennessee	66,990
Plas-Tank 16,308 gallon storage transfer tank	Plas-Tanks Industries, Inc.	Fairfield, Ohio	8,000
Plas-Tank 2,014 gallon open-head mixing tank	Same	Same	1,685
Impregnation Cell	Rothschild Boiler and Tank Works, Inc.	Shreveport, Louisiana	194,000