SULFUR COATINGS FOR MINE SUPPORT

by

John M. Dale
Allen C. Ludwig

FINAL REPORT

Project 11-3124

Contract ~~HO211062~~
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for

U. S. Department of Interior
Bureau of Mines
Spokane Mining Research Center
1430 N. Washington Street
Spokane, Washington

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SOUTHWEST RESEARCH INSTITUTE
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FOREWARD

This study was conducted by Southwest Research Institute, San Antonio, Texas under Contract HO210062 with the U.S. Department of Interior, Bureau of Mines. Technical Project Officer was Mr. Lester J. Crow of the Spokane Mining Research Center.

Inclusive dates of research were 5 June 1971, through 30 November 1972.

Southwest Research Institute personnel who were the principal contributors to this program were Mr. John M. Dale, Project Manager, Mr. Allen C. Ludwig, and Mr. Henry F. Frazier.

ABSTRACT

Sulfur is a plentiful, low cost, unique material whose physical properties can be altered and employed in structural applications. This program was undertaken to develop an optimum sulfur based formulation for use as a coating to both seal and support mine walls. The initial effort in the program was devoted to a laboratory study of the physical and mechanical properties of a variety of sulfur base coatings that were specifically formulated for this application. Concurrent with formulation development, laboratory equipment and techniques were developed for spray applying the sulfur based coatings to the ceiling and walls of a structure that simulated the interior of a mine. Much of the formulation work was guided by the experiences encountered when attempting to spray the formulations overhead.

One hundred parts of sulfur modified with 10 parts of talc, 3 parts of milled glass fiber, and 2 parts of dicyclopentadiene was found to be a fire retarded, low odor, low eye irritation, sprayable formulation for sealing and strengthening mine walls. An invention disclosure on this formulation was submitted to the Bureau of Mines and a patent application was filed. Various mineral samples were obtained and adhesive strengths of the formulation to these samples in both the wet and dry state were measured.

With the development of an attractive sulfur based coating material, attention was directed to the design, fabrication, and testing of a portable spray application unit so that coatings might be applied in the field to various rock surfaces and earth formations for further evaluation. The unit was fabricated in the Southwest Research Institute shop. Once operational, the unit's capabilities were field tested and demonstrated at three separate locations. Upon completion of the field testing, the unit was shipped to the Spokane Mining Research Center where Bureau personnel were instructed in the use of the unit.

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INTRODUCTION

The advantages and practical aspects of using sulfur as a construction material have largely been overlooked in the past in favor of using sulfur as a chemical feedstock. Recent developments in mixing sulfur with various materials, and altering its physical properties chemically, have shown it to have considerable potential for a variety of new applications. Recently a world oversupply of sulfur has developed. The Bureau of Mines has pointed out that this oversupply situation for sulfur is not merely cyclic or transient, and could become much worse if, as expected, sulfur or sulfur equivalents from various environmental related desulfurization operations flood the market. The oversupply situation has resulted in the price of sulfur dropping to its lowest level in 40 years. Thus, today there is a very real economic incentive to the use of sulfur.

The measured strength of elemental sulfur varies greatly with the method of test, e.i., the size of the specimen and the load rate. When drawn into thin filaments elemental sulfur exhibits outstanding strength properties. In the bulk form its strength is much like that of conventional Portland cement concrete, with the exception that it is strain rate sensitive. If quench cooled from above the transition temperature it exhibits its well known plastic-elastic behavior. The mechanical properties of elemental sulfur can be altered by control of the allotropic crystalline modifications through time-temperature control of the liquid and the solid.(1)

While sulfur has found use in structural applications in its elemental form, certain alterations of its properties can be very advantageous. There are various chemical modifiers which can be reacted with sulfur in small amounts that will change its strength, viscosity, surface tension, solidification temperature, adhesion, hardness, burning characteristics and other properties, thereby allowing it to perform in applications not normally associated with the use of elemental sulfur. Very significant modifications of elemental sulfur have been achieved by mechanical modification with inert fillers such as aggregates and fibers.(2-7) Sulfur-fine aggregate and sulfur-fine and coarse aggregate mixtures have been developed with compressive strengths of up to 10,700 psi.(8) Mixtures of sulfur and aggregate materials increase in strength with an increase in the sulfur content up to a point beyond which the strength declines. For most sulfur-aggregate mixtures the strength peaks at a sulfur content of between 16 and 25 percent by weight. It does not necessarily follow that high strength aggregates mixed with sulfur will give greater strengths than low strength aggregates mixed with sulfur; wetting characteristics between the sulfur and the aggregate and the cleavage form in the aggregate materials are often overriding. Sulfur aggregate mixtures that have no chemical modifying additives are much less resistant to freeze-thaw cycling than mixtures containing modifiers.

Characteristically, two phase materials are made up of materials with contrasting properties of strength and elasticity. Under an applied force a low-modulus substance stretches and deforms and distributes the stress to the high-strength component. Sulfur has a modulus in the vicinity of 1×10^6 psi. Glass and asbestos (with moduli of 10×10^6 and 24×10^6, respectively) should theoretically and do in practice greatly reinforce sulfur. Glass fibers can be used to reinforce sulfur to the extent that flexural strengths as great as 6,000 psi have been obtained. A disadvantage in the past to the use of glass fibers and asbestos fibers was that they greatly stimulated the burning characteristics of sulfur because they acted as wicking materials. Thus, one of the objectives of this project was to develop a method wherein glass fibers could be used with sulfur to benefit from their reinforcing characteristics without being penalized by their increase of the burning rate.

The laboratory work on this project was divided between a materials investigation and an investigation of methods of applications. The materials investigations involved the screening of a large number of candidate plasticizers, fillers, fibers and fire retardant materials. The screening criteria that was selected included tests for shear strength, adhesion, odor, eye irritation, sprayability, and burning. While the materials studies were underway, attention was directed to the development of application techniques and equipment so that there would be some assurance that the materials being developed would indeed be capable of being applied in a mine. Finally the better materials that had proven capacity to be applied through process equipment were optimized and characterized and a field applications unit was designed, fabricated, tested and delivered to the Bureau of Mines.

SELECTION AND SCREENING OF MATERIALS

This project was initiated by a review of the physical properties that were considered to be those most desirable from the standpoint of the proposed application. These were then compared to the physical properties of elemental sulfur. From this it was possible to identify the specific areas where attention should be directed in the selection and screening of materials. The specific areas for study were identified as:

1. Improve strength and reduce strain rate sensitivity
2. Provide thixotropy and ability to be sprayed overhead
3. Improve adhesion
4. Provide fire resistance
5. Provide low odor and eye irritation
6. Provide low permeability

After considering the various screening criteria, shear strength was selected as that physical measurement most related to the subject application and indicative of a physical property modification in the sulfur from which comparisons could be made. Shear strength per unit formulation cost was determined so that a cost benefit ratio could be obtained and compared to the various other property characteristics. For each formulation 3 coupons approximately 2 in. in diameter by 1/2 in. thick were cast as shear specimens. After aging for 7 days the shear specimens were tested by placing the specimen over a plate with a hole in the center. Atop the specimen a flat ended steel rod was aligned with the hole in the plate and a core was punched out of the specimen. This test can be realted to a mine ceiling wherein a loose fragment might be attempting to fall through a coating, thereby placing the coating in shear. A typical failed specimen for one of the higher strength composites is shown in Figure 1. The recorded strengths were then averaged.

It was concluded that the most practical means of applying the developed materials would be to spray them onto the mine walls and ceiling. Thus, the materials to be considered were limited to those which could be sprayed. A review was made of both the literature and Institute records on methods of plasticizing and modifying the properties of elemental sulfur so that it might be used as a surface coating to seal and strengthen mine walls. The different materials were selected based on their ability to either mechanically or chemically alter the sulfur properties either prior to, during or after its application. Particular emphasis was placed in the review

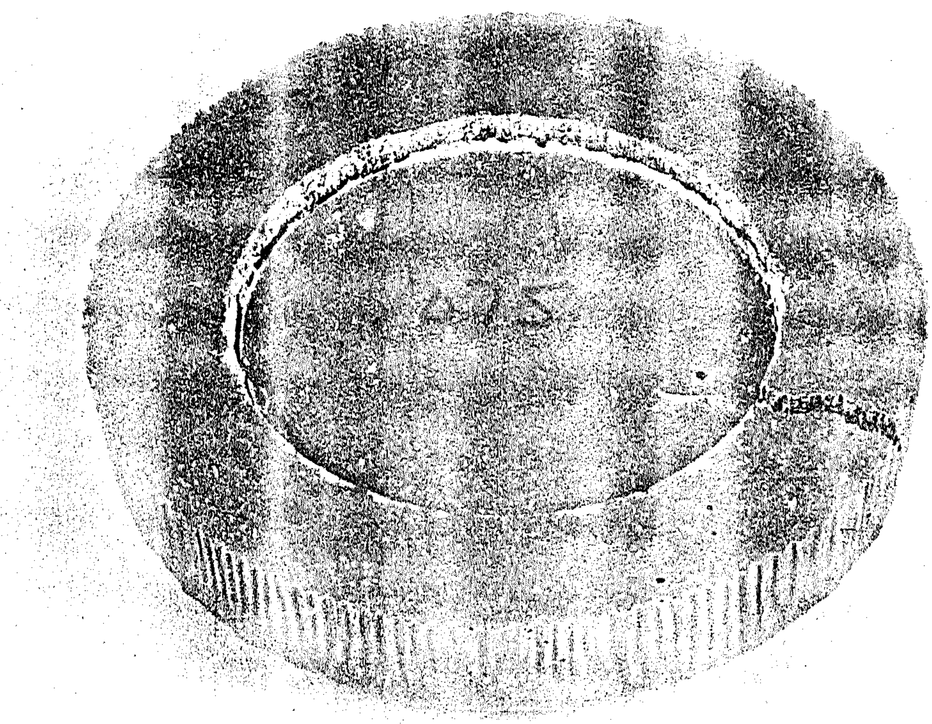

FIGURE 1 - Test Specimen After Being Tested In Shear

on the selection of those materials that combined with the sulfur and generated little or no obnoxious fumes because of the close quarters of the subject application.

Fillers

The materials selected as potential fillers included talc, clay, sand, glass beads, cement, plaster, asbestos, and milled glass fibers. Specimens were prepared initially using the maximum amount of filler that could be used without impairing the sprayability of the formulation. If the filler imparted desirable strength improvements, the content was then varied.

The performance data for the various filler materials is presented in Appendix A. It was found that the talc imparted a thixotropic nature to the sulfur, although it did not improve the shear strength. Glass beads and silica sand were tried as potential fillers, however, it was found that both of these materials segregated badly in the molten sulfur. If sufficient filler was added to overcome the segregated problem, the material was too thick to be sprayable. By adding a very fine gradation filler such as talc or silica flour in combination with the glass beads or sand, a suspension of the beads or sand was achieved and the material could be made sprayable. The sand-silica flour afforded a threefold improvement in the shear strength.

Cement and plaster were incorporated into sulfur on the basis that if these materials later hydrated, a significant strength improvement might occur in-situ. This did not occur. Clay was investigated and although a strength improvement was obtained, the clay expanded when wetted and some of the specimens disintegrated.

The most promising materials found were the glass and asbestos fibers. On a pound for pound basis the glass fibers appeared better than the asbestos. The glass fibers investigated initially were 1/8 inch milled fibers. At concentrations up to 2 parts of fiber per 100 parts of sulfur, the fibers dispersed in the sulfur without problem. At higher concentrations, however, the fibers began to agglomerate and a segregated unworkable mass resulted. It was found that talc, in addition to providing thixotropy, was very effective in dispersing the fibers. Shear strengths of 780 psi were obtained with glass fibers as compared to 120 psi for elemental sulfur. Subsequently, different types of glass fibers were obtained. Shear strengths varied from 875 to 1100 psi at the higher glass fiber loadings and this was very little improvement for the added cost involved.

CHEMICAL MODIFIERS

Another means of modifying sulfur is by the use of chemical modifiers or plasticizers. The liquid polysulfide polymers over the years have offered the most success in this area, although they are generally high cost materials. The principal disadvantage of the liquid polysulfide polymers for mine wall coatings is the odor and possible eye irritation from fumes associated with their use. Ideally the modifiers for sulfur should be odorless but more importantly the modified sulfur product should be odorless since it must be sprayed in the close environment of a mine.

A general class of sulfur modifiers that were found to be attractive for the subject application were unsaturated cyclic hydrocarbons. These materials cause crosslinking of sulfur chains and a variety of property improvements. With chemicals such as divinyl benzene or 1, 5, 9-cyclododecatriene, the crosslinking reaction is relatively hard to control such that, at concentrations as low as 3% by weight of either of these materials, gelling occurs at the higher concentrations or at temperatures considerably above the normal working temperature range of 260-300° F. These materials as well as the reaction products tend to have a disagreeable odor which is undesirable.

Dicyclopentadiene reacts with sulfur very similarly to the octadienes. While the odor of dicyclopentadiene is objectionable at elevated temperatures, when reacted with sulfur, which it does very easily, the reaction product is practically odorless and is not considered objectionable. It also improves the fire resistance of the coatings. These characteristics, plus the fact that dicyclopentadiene is available in large quantities at approximately 12¢/lb., made it very attractive as a chemical modifier for sulfur in this application.

With the recent surge of interest in sulfur product development, additional modifiers have become available on a commercial or semi-commercial basis. Chevron Chemical Company, Cities Service Company, Fike Chemical Company, and the Society Nationale Des Petroles D'Aquitaine (SNPA) (France) are examples of concerns from whom samples were requested and received.

Consideration was given to the possibility of combining different plasticizers and this was done to advantage with combinations of dicyclopentadiene and the SP-1515 plasticizer. The maximum shear strength achieved with combinations of modifiers was 515 psi as shown in Appendix A and was composed of 2 parts DCPD and 3 parts of the SP-1515 plasticizer. The strengths obtained and cost-strength rations of these combinations did not offer any advantages over some of the other formulations developed.

Combination of Fillers and Chemical Modifiers

Combinations of fillers and chemical modifiers were found to provide the best set of properties. Shear strengths of 700-900 psi were obtained by using a plasticizer in addition to glass fibers and talc. The most promising formulations were those employing 2 parts dicyclopentadiene, 3 to 5 parts glass fibers, and 7.5 to 15 parts talc. In addition to the relatively high strength - cost ratio, these formulations had desirable spraying characteristics, good adhesive properties, good fire resistance, and low odor and eye irritation. The formulations employing two plasticizers in combination did not provide any strength advantage when filled with fiber and talc.

Impregnation

Another means of improving the strength of the mine walls is by impregnation. When specimens of soil, concrete, and slate were impregnated with sulfur by submerging them in a molten bath of sulfur, a considerable improvement was made with the soil and concrete, whereas there was little change in the slate properties as indicated below:

Materials	Sulfur Absorption (% by Weight)	Shear Strength Before psi	Shear Strength After psi
Soil	19.4	70	435
Concrete	9.3	640	1490
Slate	2.7	960	995

Attempts to impregnate a soft shale material obtained locally were unsuccessful since specimens crumbled badly in drying out before they were impregnated. It is possible to coat moist to wet shale and minerals, but impregnation of moist materials with molten sulfur is most difficult unless the material is very open and porous. It is possible, for example, to impregnate a graded aggregate, even when the aggregate is wet, if the spaces between the aggregate particles are such that flow can be established.

Providing Thixotropy and Sprayability

Molten elemental sulfur in the temperature range of 240 to 320°F has a viscosity and surface tension very much like that of distilled water. In the molten state it can be pumped and sprayed with heated or preheated conventional spray nozzles in a manner identical to applying paint. For the wall coatings, however, a relatively thick coating of approximately 1/8" is generally called for. In order to prevent flow of the coating until solidification has occurred, it was found that the addition of talc imparted a thixotropic nature to the formulation. In addition, as mentioned earlier, the talc also suspended and distributed the milled glass fibers, such that the resulting mixture can be sprayed. This was a significant finding. At concentrations above 2 parts glass fibers per 100 parts sulfur, the glass fibers exfoliate and tend to lump into one large mass. Attempts to spray such a mass results in a plugged spray nozzle. By varying the talc concentration between 5 and

15 parts per 100 parts of sulfur, glass concentrations as high as 5 parts have been sprayed successfully. As the talc and glass fiber content increases, the character of the coating improves up to a point beyond which the texture at the coating begins to deteriorate and become rough and uneven. While less than 10 parts of talc looked the most promising in the laboratory , 10 parts of talc performed much better in the spraying equipment. At this concentration a smooth textured surface was obtained with a minimum of splatter and waste. This is discussed more fully in the equipment development section.

Adhesion

In the early stages of the program the adhesion of coupons of the various formulations were measured against glass and compared to elemental sulfur. Elemental sulfur has very poor adhesion to glass, and several days after being poured onto glass elemental sulfur will lose bond with the glass of its own accord. Thus, any improvement is easily discernible and this technique proved to be a rapid screening technique most useful in selecting those materials for subsequent testing where actual physical measurements were taken.

There are a variety of minerals that have a glass like surface. To measure the adhesion to various substrates the apparatus shown in Figure 2 was assembled using a hydraulic ram with a specially fabricated test carriage. Automotive valves were modified by shortening the stem and drilling holes in the heads. The valve heads were then placed into the molten formulation which had been poured or sprayed onto the adherend. After solidification the test carriage was then affixed to the stem and the heads were pulled away from the adherend. The test apparatus can be used either vertically or horizontally. The principal substrates investigated included glass, plywood, slate, and a shale available in the local area. Table I lists the adhesive strength for several formulations. Figure 3 shows three adhesion test specimens after failure. The first specimen is that of elemental sulfur on glass. Note the smooth glassy surface indicating poor adhesion. The second and third specimens were of a formulation consisting of 100 parts sulfur, 10 parts talc, 5 parts glass fibers, and 2 parts dicyclopentadiene (DCPD) adhered to shale and wet plywood respectively. Note that failure occurred through the adherend in both instances.

Laboratory Application Experience

A steam jacketed autoclave with an internal paddle arm mixer and a flexible discharge line was set up in the laboratory next to a full size walk-in paint spray booth which was lined with plywood. With this equipment it was possible to prepare batches of materials from 100 to 200 pounds in size to study the problems and develop the techniques necessary to apply the coatings. An important point was the development of the ability to spray overhead, obtain

FIGURE 2 - Adhesion Test Puller

TABLE I

Adhesion of Sulfur Formulations to Various Substrates

Formulation Parts by Wt.		Age	Substrate	Adhesive Str. (PSI)	Remarks
Elemental Sulfur		1 hr	Glass	90	
		16 hrs.	Glass	15	
100	Sulfur				
3	SP-1515	4 days	Glass	39	
		4 days	Slate	88	
100	Sulfur				
10	SP-1515	4 days	Glass	18	
		4 days	Slate	35	
100	Sulfur	4 days	Glass	32	
10	Talc	4 days	Slate	62	
5	1/8" glass fibers	3 mos.	Plywood	59	
2	DCPD	3 mos.	Plywood	47	Wetted before application
100	Sulfur	2 days	Glass	25	
10	Talc	2 days	Soft Shale	14	Failed in Shale
3	1/8" glass fibers	2 days	Med. Hard Shale	44	Failed in Shale (Shale was wet when applied)

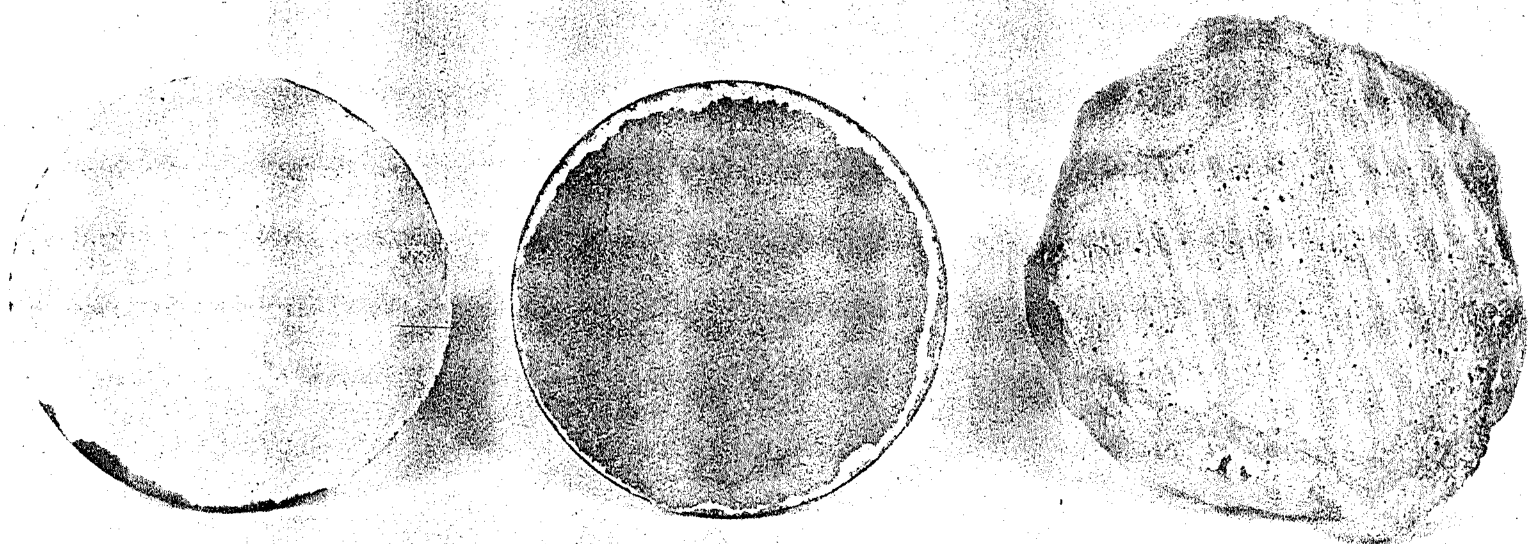

FIGURE 3 - Adhesive Test Specimens After Failure on Glass, Slate, and Plywood

uniform coverage, and have the material stay in place and not run or drip. In Figure 4 attention is being directed to a ceiling and wall coating of a formulation containing 100 parts of sulfur, 10 parts of talc, and 2 parts of dicyclopentadiene. This formulation was applied at 290°F through a 0.156 inch diameter fan spray nozzle. The spraying pressure was provided by 25 psi air pressure applied to the vapor space of the autoclave. The formulation sprayed well, adhered well to the ceiling and there was very little overspray. Immediately to the rear of the area being inspected the ceiling was coated with the same formulation, at the same temperature using the same spraying pressure, but using a 0.313 inch diameter fan spray nozzle. The added flow rate resulted in an irregular coating that was characterized by many small stalactites hanging from the ceiling.

Spraying Confined Area

The type of sulfur used plays an important role in the amount of fumes generated. Frasch process sulfur contains dissolved hydrocarbons and various sulfur-carbon complexes which vary depending upon the mine where the sulfur is obtained and the length of time the sulfur is held in the molten state. Frasch sulfur is also produced at lower temperatures than the other major type of sulfur which is recovered sulfur produced by the Claus process. Recovered sulfur generally has less hydrocarbon contaminates in it, and because it has been produced at a higher temperature it has less volatiles. At Southwest Research Institute on past projects over 100,000 pounds (45 long tons) of Frasch sulfur have been sprayed outside and fumes have never presented a problem. Their presence, however, suggested that for this project recovered sulfur be used, which it was throughout.

An airless spraying system, wherein the spraying pressure is maintained below 35 psi and the use of spray nozzles that create a spray pattern but do not overly atomize the sulfur formulation, has been found to be most desirable. The use of any atomizing air as employed in conventional paint operations is most undesirable because of the vapors and mist generated.

To determine if the vapors generated during a spraying operation in a closed environment would be objectionable, a booth which was 7 ft. high by 8 ft. wide by 8 ft. deep was equipped with an airtight clear polyethylene door, and formulations containing various amounts of dicyclopentadiene, milled glass fiber and talc were sprayed into it. It was found that if the dicyclopentadiene is reacted with the sulfur for at least 24 hours, and preferably 48 hours, no goggles or respirators are required.

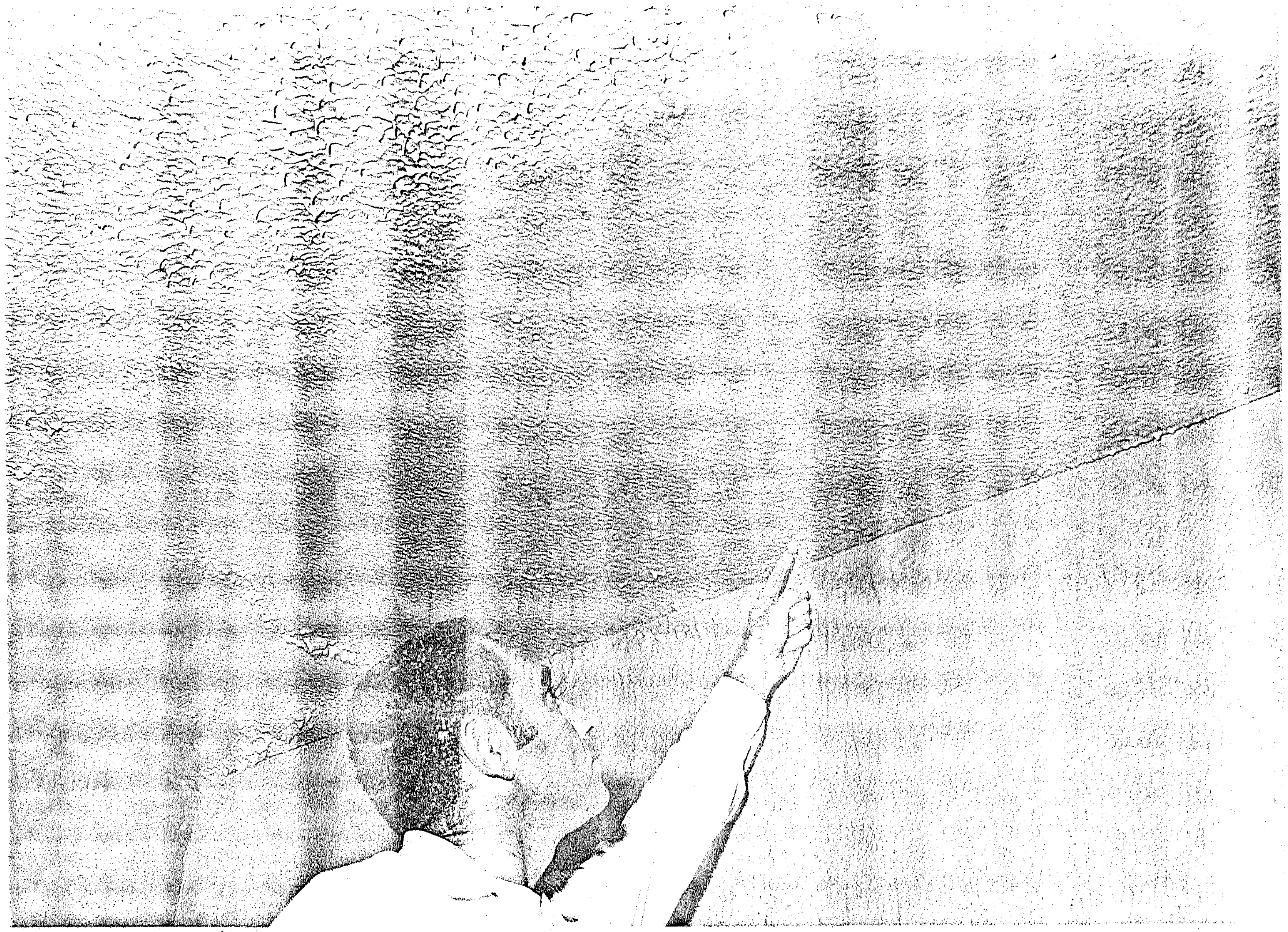

FIGURE 4 - Inspecting A Sprayed-On Overhead Sulfur Based Coating

FINAL FORMULATION OPTIMIZATION AND CHARACTERIZATION

From results of the laboratory investigation and the equipment development work, it is concluded that, for the subject application, advantage could be obtained by the addition of dicyclopentadiene, talc and glass fibers. Optimization and characterization of these materials were undertaken to arrive at the final formulation.

Dicyclopentadiene

Dicyclopentadiene is a non-conjugated diene, which as the dimer is the stable form of the conjugated diene monomer, cyclopentadiene. Dicyclopentadiene and the monomer cyclopentadiene, which can be recovered almost quantitatively by controlled thermal decomposition, are versatile chemical intermediates for synthesis of resins, polymers, elastomers, perfumes, pharmaceuticals, pesticides, fuel and lubricant additives, and other industrial chemicals. Dicyclopentadiene can be obtained from Velsicol Chemical Corporation and Enjay Chemical Company at 9 to 12 cents per pound depending upon the quantity ordered.

The reaction between dicyclopentadiene and sulfur was studied as a function of the reaction temperature, the quantity of dicyclopentadiene employed, the reaction time and the degree of fire retardency imparted to the formulation. From a practical standpoint it is desirable to have the reaction temperature and the application temperature the same, since by doing this the equipment can be set at one temperature and operational problems are reduced. Based on the laboratory work on adhesion, a temperature of 290° F appeared to give good adhesion to shale and other substrates. There is a possibility that field work applying the coatings to different substrates will result in a desire to alter this temperature either up or down. It was found that 5 parts by weight of dicyclopentadiene reacted with sulfur causes jelling of the formulation, which cannot be tolerated. However, 2 parts by weight does not cause jelling even when the temperature is raised to as high as 380° F. It was found that as the dicyclopentadiene reacts with the sulfur the color of the formulation changes to a dark brown. Dicyclopentadiene is normally added to sulfur while the sulfur is molten. There is an odor associated with the dicyclopentadiene and with the dicyclopentadiene-sulfur mixture immediately after the dicyclopentadiene has been added. This odor is more evident when the material is sprayed than when the material is held in a vessel. By reacting dicyclopentadiene with sulfur at 290° F for 24 hours or longer, its presence can no longer be detected either in the vessel or when spraying. Thus, it is important to react dicyclopentadiene with the sulfur for at least 24 hours where it is to be sprayed in a confined and poorly ventilated area, thereby avoiding the odor and fume problem. Experience in spraying in a closed environment and the burning characteristics of the formulation are discussed in detail in the subsequent section of the report.

Talc

The role of the talc in the formulation was studied more completely and it was found that while the formulations containing 7.5 parts by weight of talc were optimum from a strength standpoint, 10 parts by weight of talc was necessary to provide the consistency required so that the coatings could be sprayed onto ceilings and have them remain there and not drip. The talc also serves another very important role which is to suspend and distribute any fiber materials in the formulations. The sequence of addition for the talc is following the reaction period between the dicyclopentadiene and the sulfur.

Glass Fibers

Based on laboratory work, the milled glass fibers used as a filler improve the strength properties of the formulation, more than any of the other materials. In studying the glass fibers, it was found that the types, the length of the strands, and the sizings were important to the strength properties and the capability of being sprayed. In view of this, samples of different types of milled glass fibers were obtained from Ferro Corporation and Owens-Corning. Ferro Corporation supplied types ACME 132-0312, 661-01-025, HC-108, 653-01-1250 and 657-01-1250. Owens-Corning supplied types 630, 701, and 709.

The milled fiber concentrations were varied from 1 to 5 parts per 100 parts of sulfur. It was found that the concentration of the 0.125 inch milled fibers could not go above 2 parts per 100 parts of sulfur, without talc being added to make a sprayable material. The talc is effective in dispensing the fibers so that they will not agglomerate. An exception to this was the Ferro 661-01-026 (0.0625 inch) milled fibers which could be used in concentrations up to 50 parts of glass per 100 parts of sulfur, without the use of talc. Due to economics, this would not be practical. In varying the concentration of the milled fibers from 1 to 5 parts by weight, the 0.125 inch milled fibers, at a concentration of 3 parts by weight had the most desirable strength properties and cost.

The laboratory studies showed that the sizings on the glass fibers, also effected the strength properties. Of all the sizings studied, the Owens-Corning, 0.125 inch milled fibers No. 630 which has a starch sizing gave the most desirable strength properties. In the laboratory, it was found that 7.5 and 10 parts of talc to 100 parts sulfur gave the most workable material. But in making larger batches the 7.5 parts of talc did not make a material with enough body to spray it onto the ceilings and walls without having some overspray and splatter. In spraying the different materials it was found that the spray pattern and the orifice diameter was important to obtain a smooth textured surface. A 0.313 inch diameter fan spray nozzle was used in spraying a formulation onto the ceiling and gave an irregular coating and small stalagtites. To overcome this, a smaller orifice diameter spray head should be used. However, due to the fact that milled fibers were being used, the size to which the orifice can be reduced is somewhat limited. Attempts to spray the material with a 0.093 inch diameter orifice resulted in the milled fibers plugging the spray head. By varying the talc concentration from 10 to 15 part per 100 parts of sulfur, a thixotropic material was obtained that could be sprayed through a 0.156 inch orifice without plugging. By using talc, 0.25 and 0.50 inch glass fibers were sprayed successfully through a spray nozzle with a 0.1870 inch orifice. In spraying the different formulations it was also found that to obtain a uniform coating and a smooth textured surface, a spray nozzle with a flat spray pattern performed best.

The effect of glass fiber length and type on the shear strength was also investigated and the results are shown in Table II. Without glass fiber the formulation had a shear strength of 260 psi. Fiber length was varied from 0.025 to 0.25 inches. The different lengths and types of fibers were substituted in the basic formula of 100 parts sulfur, 10 parts talc, 3 parts glass, 2 parts dicyclopentadiene. The fibers giving the highest strength were the Owens-Corning No. 630 which have a starch sizing. Several experiments were also run wherein 0.25 inch and 0.50 inch fibers were substituted in the formulation and successfully sprayed. Some plugging difficulty was encountered with the 0.50 inch fibers, however, the use of a 0.25 inch orifice spray nozzle overcame the problem. It appears that for special applications the ability to spray formulations containing 0.50 inch fibers may be very useful.

TABLE II

Effect of Fiber Length and Type on Shear Strength
(Formula - 100 parts sulfur, 10 parts talc, 2 parts DCPD)

Weight Percent of Glass Fiber Used	Fiber Length (inches) and Type	Shear Strength (psi)
None		260
3.0	0.025 Ferro 661	240
3.0	0.031 Ferro ACME	400
3.0	0.125 Ferro 657	215
3.0	0.125 Ferro 653	445
3.0	0.125 Ferro HC	450

TABLE II (Cont'd)

Weight Percent of Glass Fiber Used	Fiber Length (inches) and Type	Shear Strength (psi)
3.0	0.125 Ferro Cat x	620
3.0	0.125 Owens-Corning 709	630
3.0	0.125 Owens-Corning 701	830
3.0	0.125 Owens-Corning 630	900
3.0	0.250 Owens-Corning 630	1135

Burning Characteristic of Developed Formulation

To gain an indication of the burning characteristics of the developed formulation a wall and ceiling were spray coated with 100 parts sulfur, 10 parts talc, 3 parts milled glass fiber and 2 parts dicyclopentadiene. A propane hand burner was directed against the wall for 30 seconds. Figure 5 is a photograph taken 5 seconds before the flame was removed. The flame characteristics of the propane torch and the sulfur formulation are such that they do not show themselves in a black and white photograph, as the flame is light blue and the products of combustion are a colorless gas. Thirty seconds after the torch was removed it was possible to take the photograph shown in Figure 6, where attention is being directed to the fact that self-extinguishing has occurred and it is possible to hold one's finger to the area where the burning had occurred.

The results described above constitute a considerable improvement over what would occur with previously developed formulations of sulfur and sulfur plasticized with conventional plasticizers such as the liquid polysulfides. Sulfur and conventionally plasticized sulfur would melt, catch fire, and the flame would be propagated by surface spread and dripping liquid, then would continue to burn and become more intensive until all of the sulfur or plasticized sulfur were consumed. If glass fiber were added to elemental sulfur or conventionally plasticized sulfur, it would burn even more rapidly as the glass fibers in previous formulations acted as a wick and stimulated burning.

Briefly, with the developed formulation the surface heats up and ignites and begins to burn, but the heat also causes the dicyclopentadiene to further crosslink and in combination with the talc and sulfur a char is formed that acts as an insulation and protects the substrate from further burning and self-extinguishing occurs. It was found that 2 parts by weight of dicyclopentadiene is effective for crosslinking and additional quantities of dicyclopentadiene do not offer any observable advantage. The more

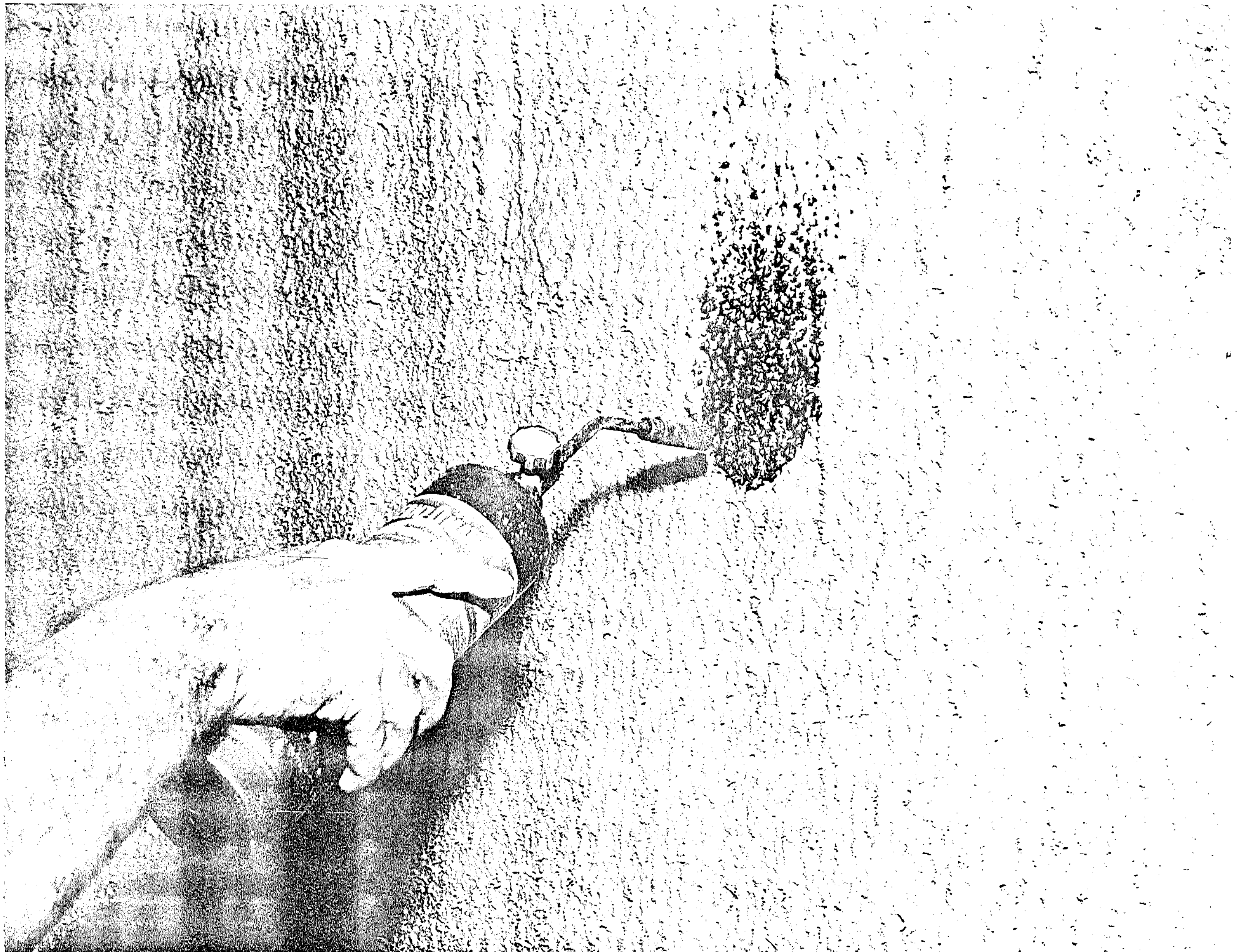

FIGURE 5 - A Propane Torch After 25 Seconds
Against the Sulfur Coating

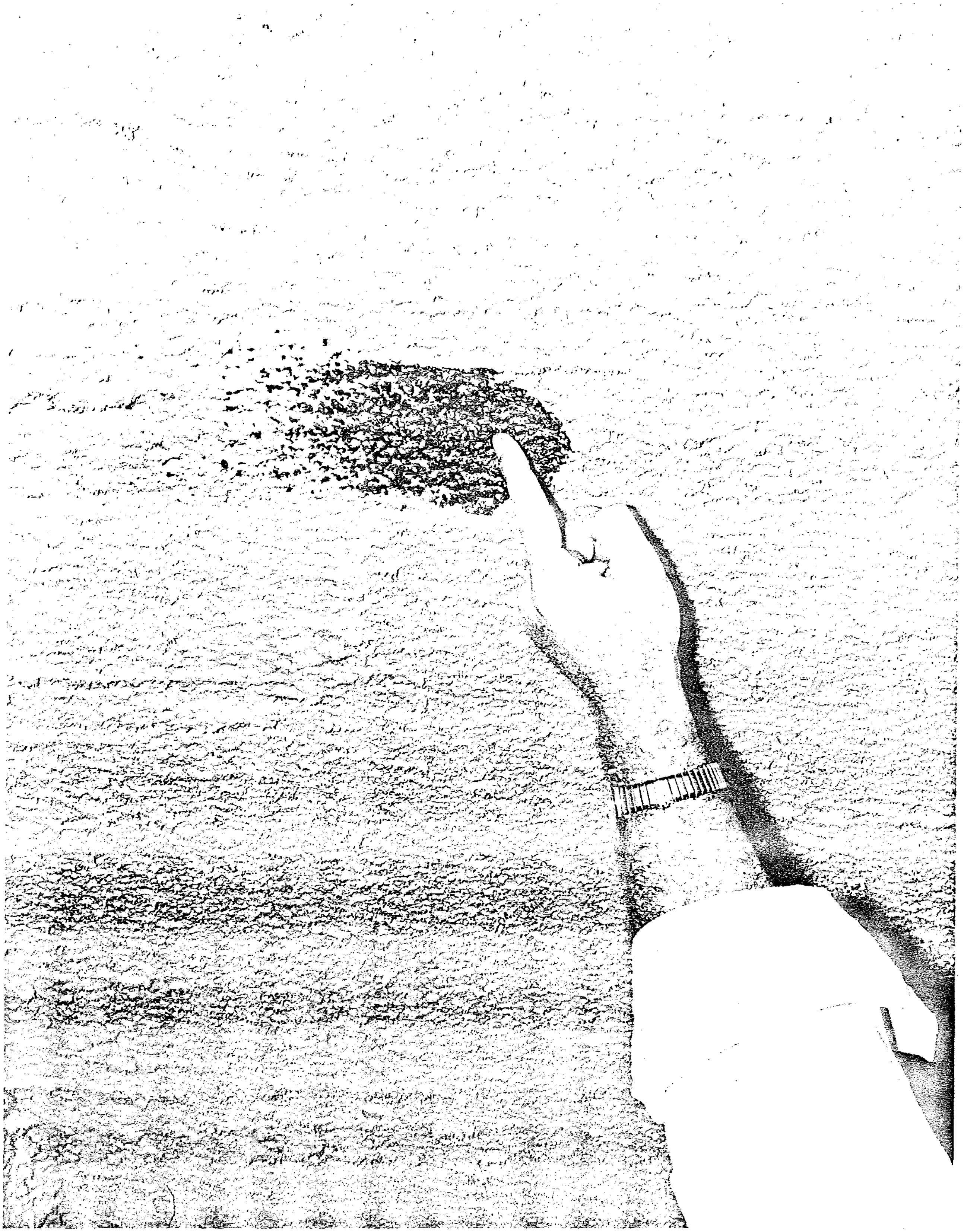

FIGURE 6 - Inspecting Charred Area

thixotropic the formulation is when it is applied, the less tendency there is for the formulation on being reheated to flow, and the more rapidly crosslinking occurs. It was found that ceiling coatings that had at least 10 parts by weight of talc resisted the tendency to flow and drip when a propane torch was applied to them. This ability of the coating to stay in place is a considerable departure from the performance characteristics of sulfur and earlier sulfur glass fiber combinations, and is considered to be a very important finding of this program and advances the state-of-the-art with regard to fire retarding sulfur compounds.[9] The coating shown in Figures 5 and 6 was applied over plywood which is an insulative material. The same coating applied over an earth formation should be even more difficult to ignite, because of the heat sink effect that is characteristic of a large mass of earth.

One of the problems encountered in this work was the lack of a standard (ASTM type) test which materials under development could be checked against to determine their potential and the probability of their acceptance.

Time-Strength Relationships

The time strength relationships were determined for specimens in both adhesion and shear. Table III lists the adhesive and shear strengths as a function of time for the developed formulation while the adhesive strength remained relatively constant the shear strength doubled after four days as opposed to the one and eight hour values. Adhesion of the formulation was determined against a flat glass surface which is considered harder to adhere to than rock or shale. The adhesive strength of the formulation is a considerable improvement over elemental sulfur which has no adhesion to glass after two days.

TABLE III

Time-Strength Relationships
for Sulfur Coating Formulation

(Formula - 100 parts sulfur, 10 parts talc, 3 parts glass, 2 parts DCPD)

Time	Adhesive Strength psi	Shear Strength psi
1 hr.	23	460
2 hr.	30	495
1 day	22	725
2 days	25	865
4 days	26	900
6 days	25	905
9 days	35	--
12 days	27	--

Vapor Permeability

The water vapor transmission, permeance and permeability were determined in accordance with ASTM C-355-64 (water vapor transmission of thick materials). These tests were conducted at an average room temperature of 75° F and an average relative humidity of 40 percent. The formulation used in preparing the test specimens was 100 parts of sulfur, 10 parts of talc, 2 parts of dicyclopentadiene and 3 parts of Owens-Corning 0.125 inch milled glass fibers No. 630. One-eighth inch and 0.250 inch thick pads were made by spraying that formulation over sand. Two specimens from each thickness were then cut from the pads. The specimens were affixed to vessels containing dessicant, and sealed with paraffin wax. The four specimens did not gain any weight during the six month test period, indicating that the coatings tested were impermeable.

Corrosion Resistance

To determine corrosion resistance of the coating formulation, shear coupons were prepared. After four days a set of controls were tested. Groups of three specimens each were then placed in 10% solutions of nitric acid, hydrochloric acid, sulfuric acid, and sodium hydroxide. Another set of control specimens are being held in the laboratory to be tested when the specimens are removed from their test solutions. The specimens were held in the corrosive solutions for 180 days after which they were removed from the solution, washed, inspected, and then tested. No visible or measured evidence of degradation was noted in the specimens.

POTENTIAL HAZARDS

The developed formulation contains not only talc and milled glass fiber, but dicyclopentadiene which is a crosslinking and fire retarding agent. Thus, the developed formulation is looked upon as being less hazardous than sulfur. There is no information on the specific hazards of the developed formulation, but since it contains 87.5% sulfur an indication of what might be expected can be derived by looking at the hazards associated with sulfur.

Sulfur is one of the most widely used raw materials in the chemical industry. Two very important references on the handling of sulfur are published by the National Safety Council, 425 North Michigan Avenue, Chicago, Illinois, 60611. They are as follows:

Data Sheet 592, Handling Liquid Sulfur - 1966
Data Sheet 612, Handling and Storage of Solid Sulfur

Briefly, sulfur is nontoxic and can be taken internally and intravenously in fairly large doses without injury. Sulfur dust and vapor are irritating to the eyes. The main hazard in handling solid sulfur is fire and dust explosions. Mixtures of sulfur dust and air ignite easily. The auto-ignition temperature of sulfur dust clouds is 374° F to 428° F for undispersed dust. The flash point (modified Cleveland open clip) is 335° F to 370° F and its ignition temperature is between 478° F and 502° F. When sulfur burns in the atmosphere, it forms sulfur dioxide. Sulfur dioxide is irritating to the eyes, nose, throat and lungs in concentrations greater than 6 to 20 parts per million. At 150 parts per million irritation is extreme. Concentrations in excess of 400-500 parts per million may result in suffocation.

Another indication of the potential hazards in the use of sulfur based coatings in mines can be drawn from experience derived from the underground mining of sulfur, which has been conducted in Sicily [10] and Japan [11] for decades. Until 1949 the Japanese experienced many fires caused by blasting. In 1950 intensive studies were made of the records of past fires and it was discovered that fires are more likely to start when there was a certain ratio between free sulfur and combined sulfur (iron sulphide) as shown in Figure 7.

To cope with this situation the following measures were initiated:

(1) When blasting ores which are likely to catch fire, the ores are watered before and after blasting.

(2) Inspection is made after blasting to discover any fire which may have started.
(3) If there is any burning, water is turned on it immediately.

Watering before and after blasting, inspection, and early discovery and extinguishing have been enforced rigidly in Japanese mines, and as a result they have been able to eliminate the fires from blasting.

The fact that sulfur is mined underground and the safety problems associated with this operation are handled in a perfunctory manner is in itself justification for considering the use of sulfur in the subject application. More work on fire retarding sulfur and its formulations is an area that was only touched on briefly in this program, and certainly needs more attention.

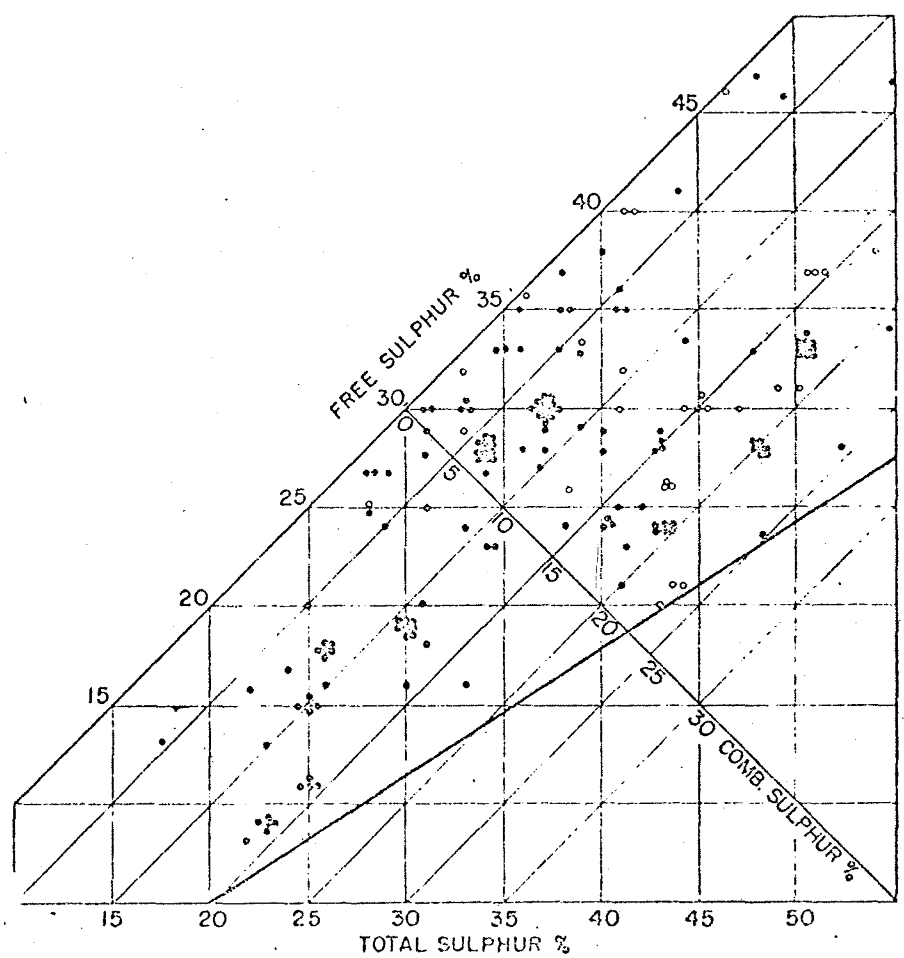

FIGURE 7 - Fire Experience in Japanese Sulfur Mines

ECONOMICS

The use of modifiers with sulfur raises the cost of the resultant materials by not only the cost of the additives, but the labor required to introduce them. When the modifiers that are available are used in large amounts, the cost of the product often overcomes the low cost advantage of sulfur which was the justification for starting with sulfur in the first place. It is not unusual to quickly exceed the value of the sulfur with the value of the additive. The following Figure 8 shows the influence of several different cost additives at different levels of addition on the cost of the sulfur additive mixture.

The specific gravity of sulfur is almost 2, whereas, many of the materials that sulfur seeks to compete with such as plastics have specific gravities in the range of 0.9 to 1.4. In most instances the sulfur composition must equate with these other materials on a volume basis rather than on a weight basis for structural reasons. Figure 9 shows how costs are altered upward when this factor is taken into consideration.

In the case of the developed formulation, the materials cost is arrived at as follows:

Components	Parts by Weight-lb	Unit Cost $/lb.	Cost $
Sulfur	100.0	$0.008	$0.80
Talc	10.0	0.035	.35
Glass (Milled Fibers)	3.0	0.300	.90
Dicyclopentadiene	2.0	0.120	.24
	115.0		$2.29

The unit cost of the formulation is, therefore, $0.02 per pound. Reducing this figure to a cost per unit volume basis and comparing it to other coating materials is done as follows:

Materials	Density lbs/cu. ft.	Unit Cost $/lb.	Material Cost $/cu. ft.
Sulfur Formulation	108	$0.02	$ 2.16
Polyester	100	0.25	25.00
Epoxy	87	0.49	42.60

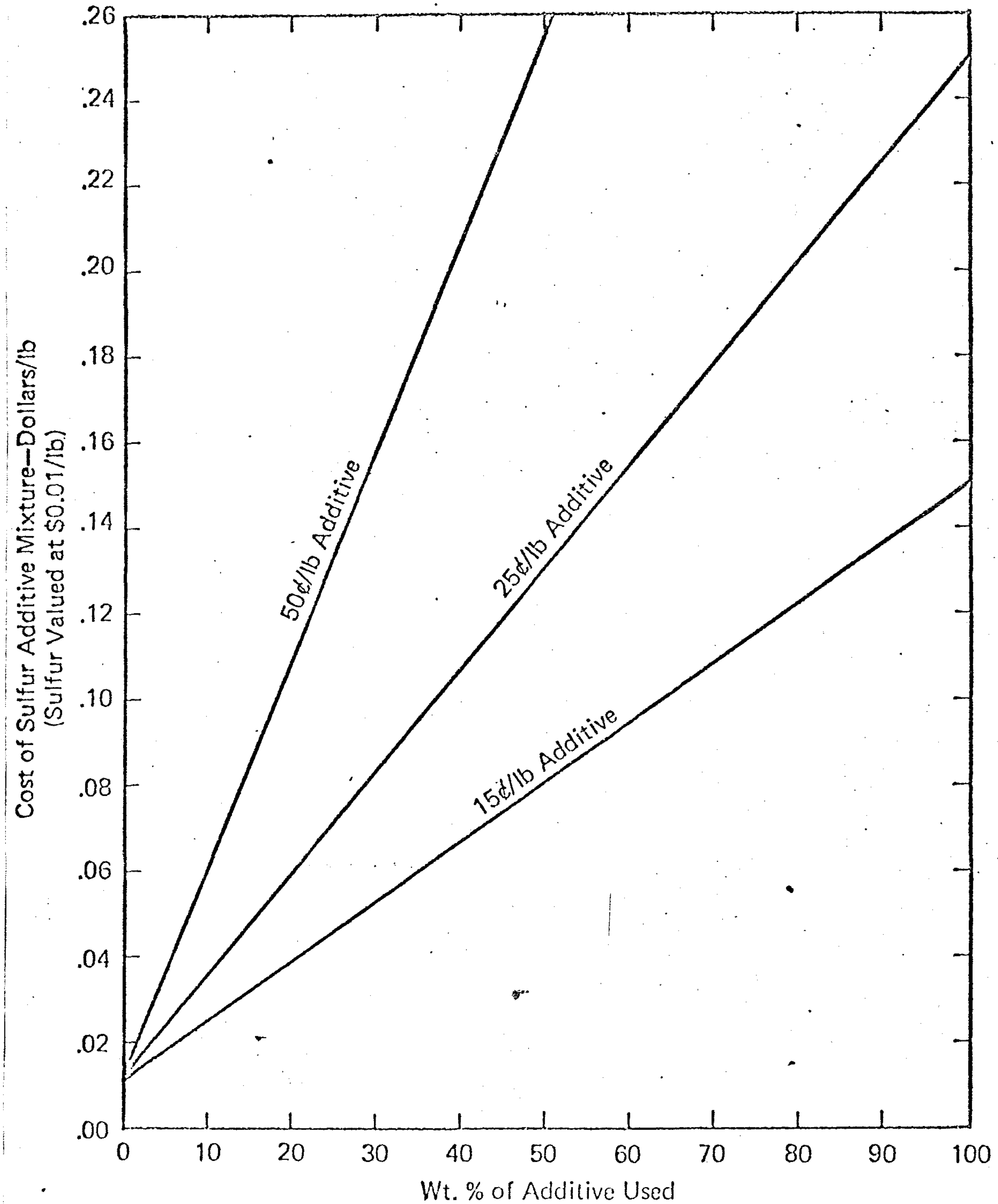

FIGURE 8 - Influence of Cost of Additive On Cost of Sulfur Additive Mixture

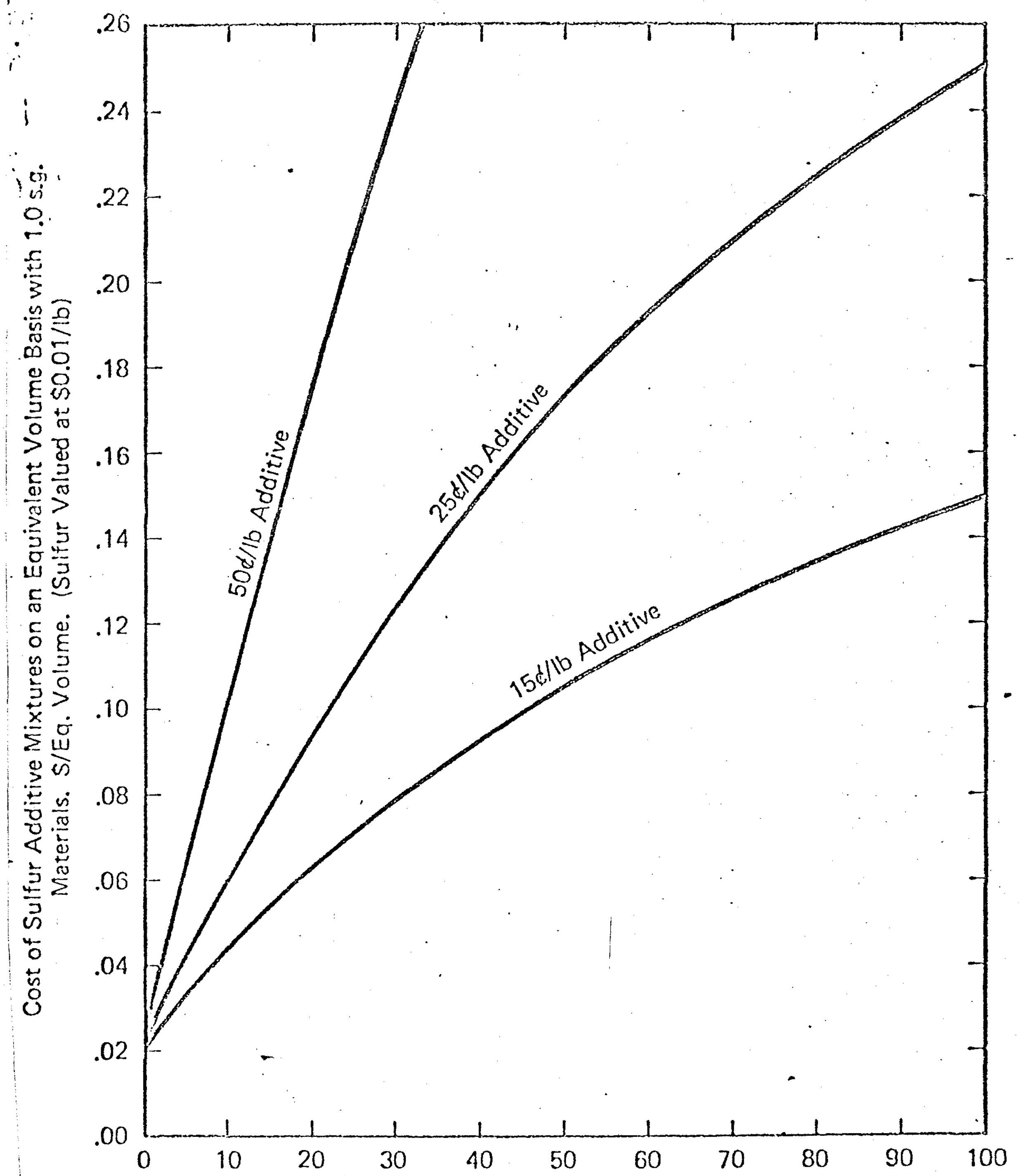

FIGURE 9 - Cost of Sulfur Mixtures Adjusted to Reflect Volume Equivalence with Less Dense Materials

There is a practical problem of obtaining a continuous "holiday free" film spray coating over an uneven surface that relates to operator skill. Since an operator must rely on visual perception in large measure to ascertain if the surface is properly sealed it is impractical to expect him to place a "holiday free" coating several thousands of an inch thick on a mine wall. Rather, the coating must be applied freely and in whatever quantity is necessary to fill all cracks, fisures, pits, and other discontinuities that exist on the mine wall face. For this reason, practical coatings are considered to vary between 0.0625 and 0.250 of an inch in thickness. This implies that the cost of the coating must be low enough that it's use will be within reason. The cost per square foot of coatings is calculated as follows:

	Material Cost per Square Foot ($/Ft.^{2})		
Material	0.062 in. Coating	0.125 in. Coating	0.250 in. Coating
Sulfur Formulation	$0.011	$0.022	$0.044
Polyester	0.130	0.260	0.520
Epoxy	0.220	0.440	0.880

Experience in the laboratory suggests that a practical coating thickness is 0.125 inch.

It requires about 145,000 BTU per long ton or 65 BTU per pound to convert dry solid sulfur at 70° F to liquid sulfur at 285° F.[12] Assuming a thermal efficiency of 30% and fuel at $0.50 per million BTU then it costs approximately $0.24 per long ton or $0.00001 per pound to melt sulfur. This does not add significantly to the cost of the sulfur coatings. There is insufficient data available at this time with which to estimate the application and final in-place cost.

FIELD APPLICATION EXPERIENCE

So that the developed formulation might be taken into the field and applied to various rock and earth formulations for further evaluations, it was necessary that a portable field applications unit be designed and built. The salient design characteristics of the unit are listed below:

1. Capacity of 600 pounds.
2. Skid mounted with wheels.
3. Jacketed and insulated.
4. Gas fired - adaptable to conversion to electric power.
5. Test pressure of 40 psi.
6. Heated discharge lines.
7. Self-contained compressed air supply.
8. Self-contained motor driven agitator.
9. Ability to spray coatings and prepare grout materials.
10. Automatic temperature controls.

The unit was designed and fabricated at Southwest Research Institute. Figure 10 is a photograph of the completed unit. Figure 11 is a photograph of the unit being used to apply a spray coating of the developed formulation to a small dam. Figure 12 is a photograph of the unit being used to grout a bank of aggregate.

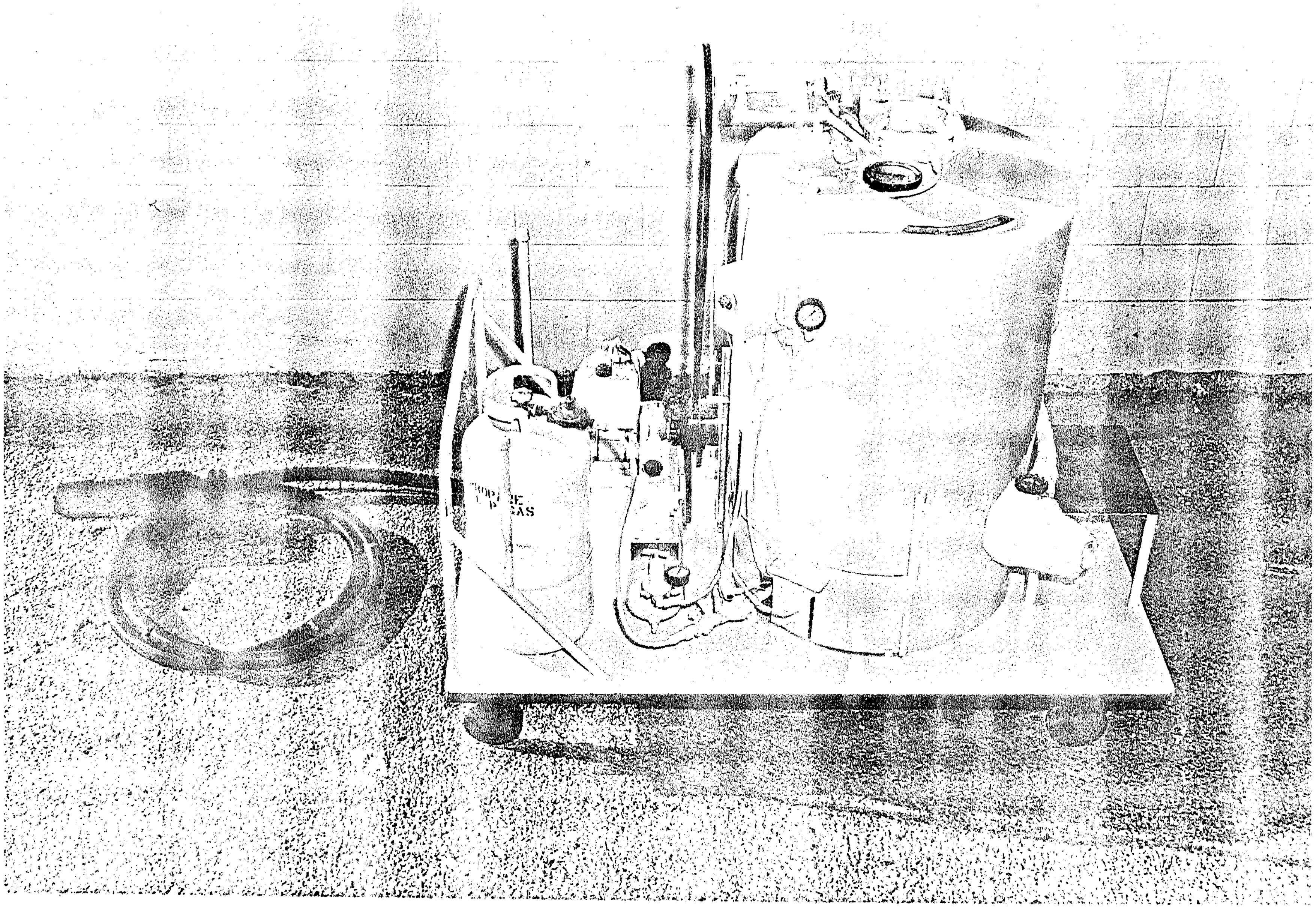

FIGURE 10 - Photograph of Sulfur Field Applications Unit

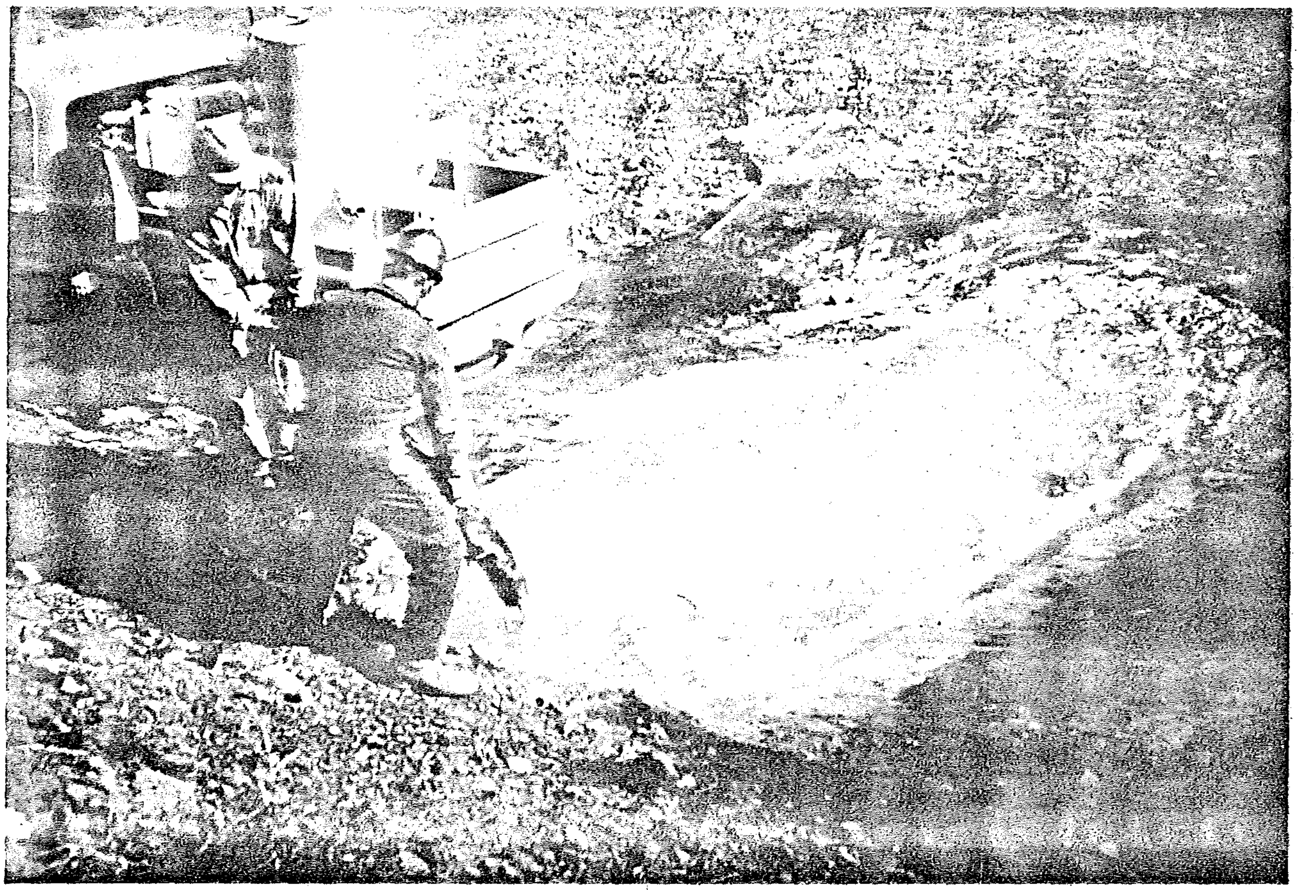

FIGURE 11. SULFUR APPLICATIONS UNIT BEING USED TO APPLY SPRAY COATING

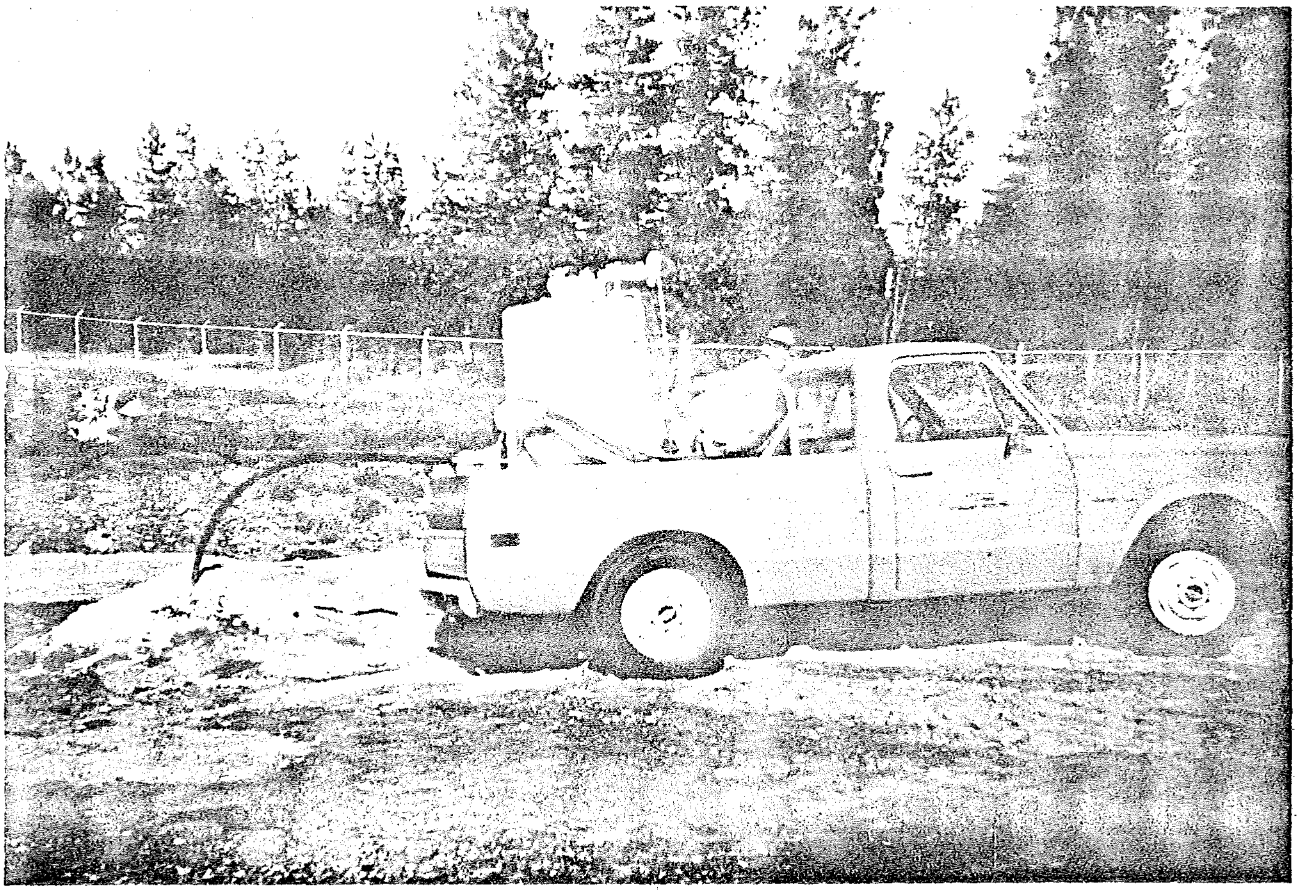

FIGURE 12. SULFUL APPLICATIONS UNIT BEING USED TO GROUT AN AGGREGATE BANK

INVENTION DISCLOSURE

An Invention Disclosure on the developed formulations was prepared on Southwest Research Institute Form OP2, dated October 28, 1971, and submitted to the Patent Advisory Committee of the Institute and the Bureau of Mines. It was assigned Institute Docket Number 1023. Subsequently, Department of the Interior "Invention Disclosure Contractor" Form 111-1217 (April 1965) was received, completed, and returned to the Department of the Interior on November 1, 1971. On July 28, 1972, a Patent Application written by the Patents Branch of the Department of the Interior was received for review. The application was reviewed and returned to the Patents Branch on August 1, 1972.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Improvements were made in the shear and adhesive strength, strain rate sensitivity, fire resistance, impermeability, and other characteristics of sulfur and its compositions in the process at developing a sealing and reinforcing coating for mine walls.

2. The formulation developed consists of 100 parts of sulfur, 10 parts of talc, 3 parts of milled glass fiber, and 2 parts of dicyclopentadiene.

3. The material costs of the developed formulation is approximately \$0.02 per pound.

4. The developed formulation can be spray applied to overhead as well as other surfaces.

5. The developed formulation can be prepared and dispersed from a completely self-contained portable applications unit at remote sites.

6. The developed coating would appear to have a considerable potential for a variety of other applications, such as ground coatings for dams, spillways, catch basins, tailings stabilization, etc.

Recommendations

1. More effort should be directed to methods of fire retarding elemental sulfur and sulfur formulations.

2. Definitive fire tests should be developed or adopted for the screening of mine wall coatings.

3. Efforts should be directed to taking the developed formulations underground to demonstrate their usefulness there.

4. A large multipurpose applications unit should be constructed for applying the developed coating in a variety of above ground mining operations.

REFERENCES

1. "Mechanical Properties of Sulphur Allotropes," by John M. Dale and Allen C. Ludwig, presented at a Colloquim on Sulfur Allotropes, sponsored by Lawrence Radiation Laboratory, University of California and The Sulphur Institute at Berkeley, July 8, 9, 10, 1964. Materials Research and Standards - Bulletin of the American Society for Testing and Materials, 5, 8, pp. 411 - 417, August 1965.

2. "Feasibility Study for Using Sulphur-Aggregate Mixtures as a Structural Material," by John M. Dale and Allen C. Ludwig, Technical Report No. AFWL-TR-66-57, Research and Technology Division, Air Force Systems Command, September 1966.

3. "Advanced Studies of Sulphur - Aggregate Mixtures as Structural Materials," by John M. Dale and Allen C. Ludwig, Technical Report AFWL-TR-68-21, Air Force Weapons Laboratory, October 1968.

4. "Sulphur-Aggregate Concrete," by John M. Dale and Allen C. Ludwig, Civil Engineering, 37, 12, December 1967.

5. "Sulphur-Fibre Coatings," by John M. Dale, The Sulphur Institute Journal, pp. 11-13, September 1965.

6. "Demonstration of Sulphur as a Load Bearing Material," by John M. Dale, Technical Report AFAPL-TR-66-151, Air Force Aero Propulsion Laboratory, Air Force Systems Command, February 1967.

7. "Investigation of Sulphur as a Structural Material," by John M. Dale, Jerry V. Fox, and Allen C. Ludwig, Technical Report AFAPL-TR-68-95, Air Force Systems Command Aero Propulsion Laboratory, August 1968.

8. "Strengths of Sulfur-Basalt Concrete," by Lester J. Crow and Robert C. Bates, Bureau of Mines, Report of Investigations 7349, March 1970.

9. "Fire Retarding Elemental Sulfur," by John M. Dale and Allen C. Ludwig, Journal of Materials, Vol. 2, No. 1, March 1967.

10. "Geology and Isotopic Studies of Sicilian Sulfur Deposits," by G. Dessau, M. L. Jensen, and N. Nakai, Economic Geology, Vol. 57, pp. 410-438, 1962.

References (Cont'd)

11. "Japan's Matsuo Sulphur Mine is Big Underground Producer," by Yoshinzo Fujita, Engineering and Mining Journal, Vol. 157, No. 8.

12. Freeport Sulphur Handbook, Freeport Minerals Company, 1959.

APPENDIX

PERFORMANCE CHARACTERISTICS OF SELECTED FORMULATIONS

Specimen	Sulfur (Parts by Weight)	Additive	Additive	Additive	Cost $/lb	Odor	Eye Irritation	Adhesion to Glass	Shear Strength (psi)	Sprayability	Viscosity Control	Shear Strength/ Unit of Cost psi/¢
1	100				.01	None	None	Poor	120	Yes	No	120
2	85	15 Talc			.014	None	None	Poor	130	Yes	Yes	93
3	70	25 Glass Beads	5 Talc		.033	None	None	Poor	75	Yes	Yes	23
4	65	23 Sand	12 0-15M Silica Flour		.0082	None	None	Poor	325	Doubtful	Yes	395
5	70	30 Cement			.01	None	None	Poor	225	Yes	Not at this concentration	225
6	80	20 Asbestos			.028	None	None	Poor	555	No	Some	198
7	77	17 Atatic Polyprop.	6 ZnS		.043	None	None	Fair	130	Doubtful	Yes	30
8	70	30 Clay			.0090	None	None	Poor	335	Yes	Yes	372
9	77	23 Gypsum Plaster			.019	None	None	Poor	150	Yes	Yes	79
10	100	1 Milled Glass			.013	None	None	Poor	280	Yes	Yes	217
11	100	2 Milled Glass			.016	None	None	Poor	425	Yes	Yes	271
12	100	3 Milled Glass	5 Talc		.019	None	None	Poor	425	Yes	Yes	221
13	100	4 Milled Glass	5 Talc		.022	None	None	Poor	785	Yes	Yes	360
14	100	5 Milled Glass	5 Talc		.026	None	None	Poor	780	No	Yes	300
15	100	3 Milled Glass	10 Talc		.02	None	None	Poor	500	Yes	Yes	251
16	100	20 Milled Glass			.058	None	None	Poor	875	No	Yes	151
17	100	30 Milled Glass			.077	None	None	Poor	900	Yes	Yes	117
18	100	50 Milled Glass			.107	None	None	Poor	1100	No	Yes	103
19	100	1 DCPD (Dicyclopentadiene)			.011	None	None	Poor	130	Yes	No	118
20	100	2 DCPD			.012	Slight	None	Good	245	Yes	No	220

PERFORMANCE CHARACTERISTICS OF SELECTED FORMULATIONS

Speciman	Sulfur	Additive (Parts by Weight)	Additive	Additive	Cost $/lb	Odor	Eye Irritation	Adhesion to Glass	Shear Strength (psi)	Sprayability	Viscosity Control	Shear Strength/ Unit of Cost psi/¢
21	100	3 DCPD			.013	Yes	None	Good	195	Yes	No	150
22	100	4 DCPD			.014	Yes	Slight	Good	155	Yes	Yes	111
23	100	5 DCPD			.015	Yes	Slight	Good	215	Yes	Yes	143
24	100	2 COT (Cyclooctene)			.024	Yes	Yes	Good	120	Yes	No	50
25	100	5 COT			.043	Yes	Yes	Good	180	Yes	No	42
26	100	10 COT			.077	Yes	Yes	Excellent	92	Yes	No	12
27	100	20 COT			.13	Yes	Yes	Excellent	180	Yes	No	14
28	100	2 R-7* (Rocure-7)			*	Slight	Slight	Poor	185	Yes	No	--
29	100	3 R-7			*	Slight	Slight	Poor	175	Yes	No	--
30	100	2 Chevron *			*	Yes	Yes	Poor	95	Yes	No	--
31	100	5 Chevron			*	Yes	Yes	Poor	110	Yes	No	--
32	100	10 Chevron			*	Yes	Yes	Fair	115	Yes	No	--
33	100	3 SP-1515 *			*	No	No	Poor	175	Yes	No	--
34	100	5 SP-1515			*	No	No	Poor	260	Yes	No	--
35	100	10 SP-1515			*	No	No	Good	265	Yes	No	--
36	100	2 DCPD	3 SP-1515		*	Slight	No	Fair	485	Yes	No	--
37	100	2 DCPD	5 SP-1515		*	Slight	No	Poor	515	Yes	No	--
38	100	2 DCPD	2 R-7		*	Slight	Slight	Poor	425	Yes	No	--
39	100	2 DCPD	2 COT		.018	Slight	None	Good	335	Yes	No	186
40	100	1.5 DCPD	15 Talc		.015	Slight	None	Good	260	Yes	Yes	173

PERFORMANCE CHARACTERISTICS OF SELECTED FORMULATIONS

Speciman	Sulfur	Additive (Parts by Weight)	Additive	Additive	Cost $/lb	Odor	Eye Irritation	Adhesion to Glass	Shear Strength (psi)	Sprayability	Viscosity Control	Shear Strength Unit of Cost psi/¢
41	100	2 DCPD	1 Glass		.015	Slight	None	Good	485	Yes	No	322
42	100	2 DCPD	1 Glass	5 Talc	.016	Slight	None	Good	530	Yes	Yes	332
43	100	2 DCPD	3 Glass	5 Talc	.0210	Slight	None	Good	760	Yes	Yes	351
44	100	2 DCPD	3 Glass	7.5 Talc	.021	Slight	None	Good	810	Yes	Yes	386
45	100	2 DCPD	3 Glass	10 Talc	.023	Slight	None	Good	800	Yes	Yes	347
46	100	2 DCPD	3 Glass	15 Talc	.025	Slight	None	Good	555	Yes	Yes	222
47	100	2 DCPD	5 Glass	10 Talc	.026	Slight	None	Good	895	No	Yes	339
48	100	2 R-7 2 DCPD	5 Glass	10 Talc	*	Slight	None	Good	735	Maybe	Yes	--
49	100	2 DCPD	(.025 in.) 5 Glass	10 Talc	.026	Slight	None	Fair	240	Yes	Yes	92
50	100	2 DCPD	(.0312 in.) 5 Glass	10 Talc	.026	No	None	Fair	400	Yes	Yes	154
51	100	2 DCPD	(.125 HC) 5 Glass	10 Talc	.026	No	None	Poor	545	Yes	Yes	210
52	100	2-1,5 Cyclooctadiene	(.125 in.) 5 Glass	10 Talc	.037	Yes	Slight	Fair	635	Maybe	Yes	172
53	100	2-1,5 Cyclooctadiene	(.125 in.) 5 Glass	10 Talc	.037	Yes	Slight	Poor	345	Maybe	Yes	93
54	100	2 DCPD	3 Glass	7.5 Talc	.021	No	None	Excellent	495 at 1 hr.	Yes	Yes	236
55	100	2 DCPD	3 (Ferro) (Cat-x)	7.5 Talc	.021	No	None	Excellent	440 at 1 day	Yes	Yes	210
56	100	2 DCPD	3 Glass	7.5 Talc	.021	No	None	Excellent	725 at 1 day	Yes	Yes	344
57	100	2 DCPD	3 Glass	7.5 Talc	.021	No	None	Excellent	700 at 7 days	Yes	Yes	334
58	100	2 DCPD	3 Glass	7.5 Talc	.021	No	None	Excellent	460 at 8 hrs.	Yes	Yes	219

PERFORMANCE CHARACTERISTICS OF SELECTED FORMULATIONS

Speciman	Sulfur	Additive (Parts by Weight)	Additive	Additive	Cost $/lb	Odor	Eye Irritation	Adhesion to Glass	Shear Strength (psi)	Sprayability	Viscosity Control	Shear Strength/ Unit of Cost psi/¢
59	100	4 DCPD	3 Glass	7.5 Talc	.022	Slight	None	Good	715	Yes	Yes	325
60	100	2 DCPD	1=1/2Glass	10 Talc	.017	No	None	Excellent	740	Yes	Yes	435
61	100	2 DCPD	3 Glass Cat-x	7.5 Talc	.021	No	None	Excellent	620 at 4 days	Yes	Yes	295
62	100	2 DCPD	3 Glass (653)	10 Talc	.023	No	None	Excellent	445 at 7 days	Yes	Yes	193
63	100	2 DCPD	3 Glass (657)	10 Talc	.023	No	None	Good	215 at 7 days	Yes	Yes	93
64	100	2 DCPD	3 Glass (630)	10 Talc	.023	No	None	Excellent	900 at 4 days	Yes	Yes	391
65	100	2 DCPD	3 Glass (701)	10 Talc	.023	No	None	Excellent	830 at 4 days	Yes	Yes	360
66	100	2 DCPD	3 Glass (709)	10 Talc	.023	No	None	Excellent	628 at 4 days	Yes	Yes	273
67	100	2 DCPD	3 Glass (630-.25 in.)	10 Talc	.023	No	None	Excellent	1135 at 4 days	Yes	Yes	495
68	100	2 DCPD	5 Glass (630-.25 in.)	10 Talc	.026	No	None	Excellent	1045 at 4 days	No	Yes	402