HILGARDIA

CONTENTS

SOME FACTORS AFFECTING THE BURNING OF SULFURS USED IN SULFURING FRUITS

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DURING THE 1936 season, growers in various districts in California were experiencing some difficulty in sulfuring the fruit to be dried. Long, Mrak, and Fisher[5] found that the difficulties of that season were merely a recurrence of a series of yearly troubles. These investigators determined that some of the samples of sulfur in question burned 90 to 100
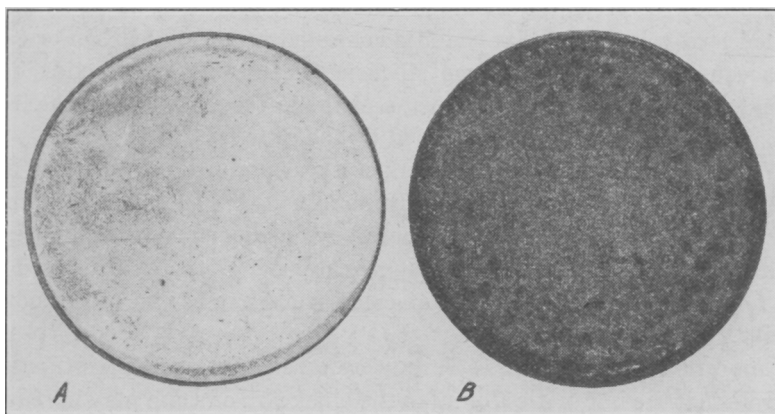

Fig. 1.—Illustrations of slag resulting from incomplete burning: *A*, light-colored slag from a high-grade sulfur indicating that the fire was smothered through insufficient ventilation; *B*, dark-colored slag from a low-grade sulfur indicating that the fire was smothered by carbon or carbonaceous matter which floated to the surface of the molten sulfur.

per cent, whereas many others burned anywhere from 10 to 50 per cent. With the poor-burning sulfurs the result was reduced quality of the product, delay in operations during the drying season, and an actual loss of sulfur through failure to burn.

Poor-burning sulfurs develop, over the burning, molten surface, a black film that decreases the rate of vaporization of the sulfur by shielding the molten sulfur from direct contact with the flame, which grad-

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ually decreases the burning area and finally extinguishes the flame. The unburned sulfur solidifies on cooling and forms a dark hard cake or slag (fig. 1), not easily removed from the pans.

Though a black variety of sulfur can be produced,[6] the sulfur samples tested in the experiments reported here were not subjected to the same conditions as those given for producing the black variety.

EXPERIMENTAL RESULTS

Identification of Contaminants Affecting Burning.—Chemical tests on the composition of this black film on cakes from commercial sulfuring houses showed, after the included sulfur had been driven off by controlled heat treatment, that the film consisted largely of carbon or carbonaceous material, with some siliceous matter and iron oxide, the second probably coming from dust, and the latter chiefly from the iron pans in which the sulfur was burned by the growers.

When this work was first undertaken it was planned to be carried out entirely in the laboratory. The results obtained were such, however, that it was decided to follow up the laboratory experiments with field tests conducted in a commercial sulfuring house. All of the sulfurs used in the following experiments were of commercial grade and of unknown purity.

Laboratory Experiments.—Tests were directed toward investigating the role that the impurities found in the black film or scum play in reducing the burning of sulfurs. The method consisted in adding varying small amounts of iron oxide, siliceous compounds, and carbonaceous matter to samples of sulfur no. 1 that normally burned 99.7 per cent, and observing how these added materials affected the reduction of the amount of sulfur burned.

In working out the procedure to be followed in these tests, it was found that the methods adopted would be empirical. That is, the results would depend considerably on factors influencing the temperature of the sulfur and the film formation—for example, the size of the sample used; the control of air drafts; the size, shape, and composition of the container; and the nature of the surface on which the container was placed (transite, wood, sand, and the like).

In a series of tests, 10-gram samples of sulfur gave the most consistent results. These tests also showed that 2.5-inch porcelain evaporating dishes are more satisfactory than 2-inch straight-sided aluminum dishes for the burning of sulfur. Transite board proved to be the most satis-

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[6] Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry. Vol. 10, p. 34. Longmans, Green and Company, New York, N. Y. 1930.

factory support for the sulfur dishes. Careful shielding of the containers
was necessary to insure consistently good burning.

All samples were burned from a cold start (except where noted) under
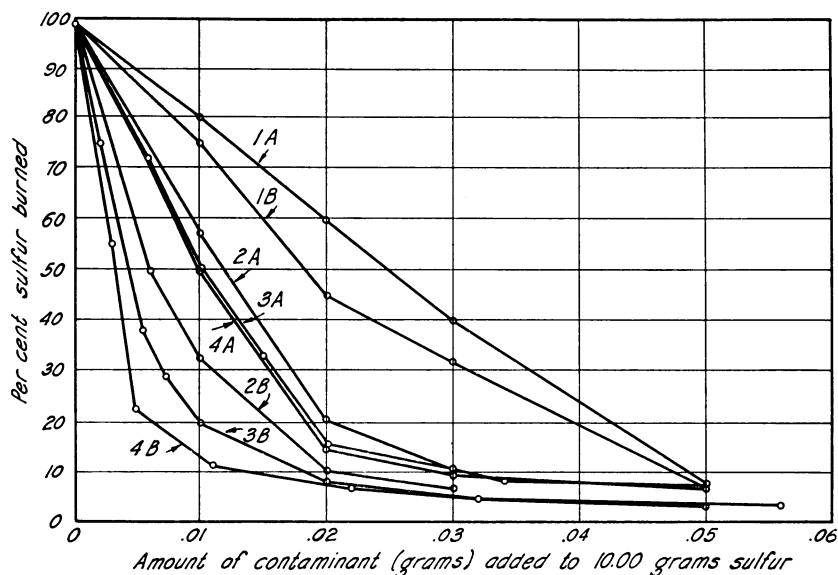optimum conditions. That is, the cold sulfur was carefully lighted with

Fig. 2.—Effect of lubricating oil (medium) and of fuel oil on the
percentage of sulfur burned:

Curve 1*A*, fuel oil added; burned at once without mixing.
Curve 2*A*, fuel oil added; burned after one thorough mixing.
Curve 3*A*, fuel oil added; burned after 4 hours and three thorough mixings during
  the interval.
Curve 4*A*, fuel oil added; burned after 24 hours and four thorough mixings during
  the interval.
Curve 1*B*, lubricating oil added; burned at once without mixing.
Curve 2*B*, lubricating oil added; burned after one thorough mixing.
Curve 3*B*, lubricating oil added; burned after 4 hours and three thorough mixings
  during the interval.
Curve 4*B*, lubricating oil added; burned after 24 hours and four thorough mixings
  during the interval.

a match, the match discarded, and the dish then placed on a transite
board and shielded from drafts.

Effect of Various Admixtures on Burning.—In the first experiments
on the effect of impurities on sulfur burning, small amounts of ignited
dust or iron oxide, varying from 0.005 to 0.05 gram, were mixed with
10-gram samples of sulfur no. 1, and the mixtures burned. These contami-
nants in the quantities used did not significantly affect the burning of
the sulfur. Judging from these results, tests would have to be confined

to a study of the difficulty originating from the presence of carbonaceous matter in commercial sulfurs.

In order to determine how molten sulfur affects the volatile vapors of carbon compounds, hot vapors from boiling fuel oils were bubbled through hot molten sulfur in a test tube. The sulfur darkened quickly;
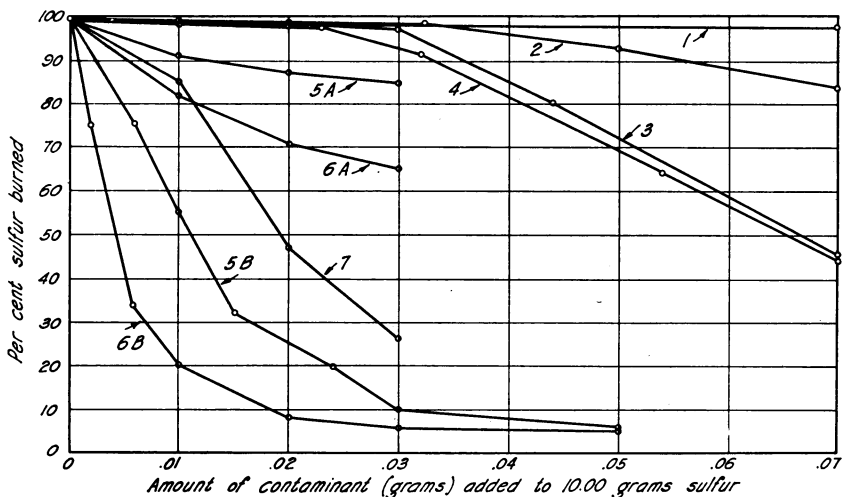

Fig. 3.—Effect of sack lining, burlap sacking, newspaper, sawdust, linseed oil, and rosin on the percentage of sulfur burned:

Curve 1, sack lining added (finely cut); burned after 1 hour with one thorough mixing.
Curve 2, burlap sacking added (finely cut); burned after 1 hour with one thorough mixing.
Curve 3, newspaper added (finely cut); burned after 1 hour with one thorough mixing.
Curve 4, sawdust added; burned after 1 hour with one thorough mixing.
Curve 5A, linseed oil added; burned at once without mixing.
Curve 5B, linseed oil added; burned after 4 hours with three thorough mixings during the interval.
Curve 6A, rosin dust added; burned at once without mixing.
Curve 6B, rosin dust added; burned after 4 hours with three thorough mixings during the interval.
Curve 7, paraffin added (finely cut); mixed in, and burned after 3 hours.

and a black film was formed over the sulfur and on the sides of the test tube above the sulfur, clearly indicating the breakdown of the fuel-oil vapors in their passage through the hot sulfur. With these results as a basis, various types of materials (lubricating oil, fuel oil, kerosene, gasoline, linseed oil, turpentine, rosin, organic acids, sawdust, paper scraps, sacking, and the like) were added to 10-gram samples of sulfur no. 1, and the resulting mixtures were burned. Some of these mixtures were burned immediately without mixing, whereas others were mixed and allowed to stand as described in figures 2 to 4.

Figure 2 shows the effect of adding varying amounts of lubricating oil (medium) and fuel oil to sulfur no. 1. As the curves show, the more thoroughly the added materials are mixed with the sulfur and the longer the time allowed for diffusion of the added substances, the lower is the percentage of sulfur burned; the greatest decrease occurred in mixtures
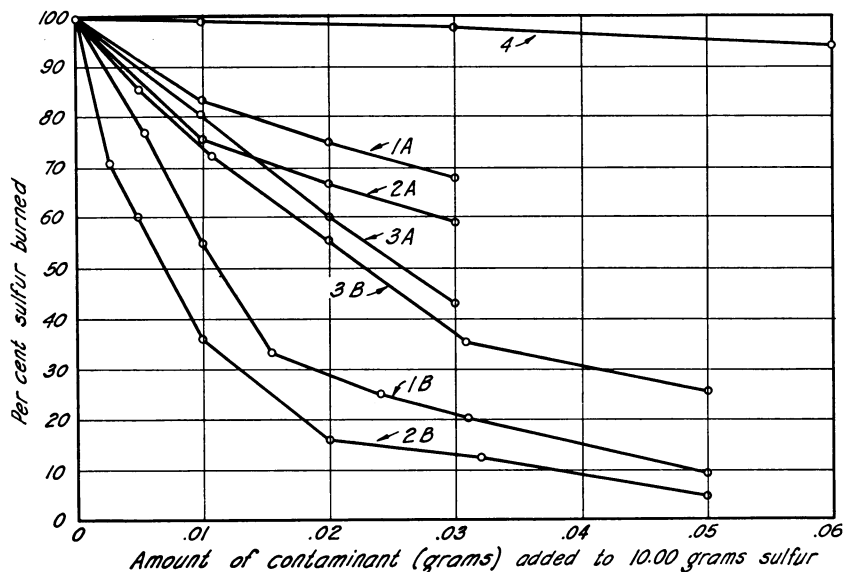

Fig. 4.—Effect of gasoline, turpentine, oleic acid, and stearic acid
on the percentage of sulfur burned:

Curve 1*A*, stearic acid added; burned at once without mixing.
Curve 1*B*, stearic acid added; burned after 4 hours and after three thorough
mixings during the interval.
Curve 2*A*, oleic acid added; burned at once without mixing.
Curve 2*B*, oleic acid added; burned after 4 hours and after three thorough mixings
during the interval.
Curve 3*A*, turpentine added; burned at once without mixing.
Curve 3*B*, turpentine added; burned after 4 hours and three thorough mixings
during the interval.
Curve 4, gasoline added; burned after 2 hours and two thorough mixings during
the interval.

where the weight of the added impurity was less than 0.01 gram. The slope of the curve gradually decreased when amounts up to 0.05 gram were added. In appearance and in effect on burning, the film or scum formed by these materials resembles that observed when low-grade commercial sulfurs were burned.

Figure 3 manifests a marked difference in the effect of certain added materials on the reduction of the percentage of sulfur burned. The curves for linseed oil and rosin show much the same slope as the oils in figure 2.

They show the same large initial drop in percentage of sulfur burned when very small amounts are added and well mixed in, and a much smaller drop when larger amounts up to 0.05 gram are added.

The picture is very different for the other materials in figure 3—when sack lining, newspaper scraps, burlap sacking, and sawdust are added. Sack lining, used by some sulfur companies to line burlap sacks for the better protection of their product, had very little effect on the burning
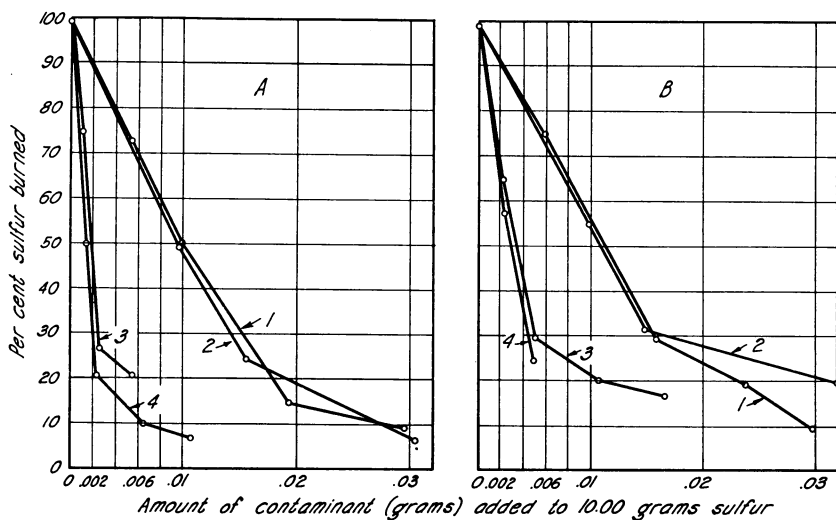

Fig. 5.—*A*, Effect of fuel oil on the percentage of sulfur burned:

Curve 1, laboratory test, in 1938, with sulfur no. 1.
Curve 2, laboratory test, in 1940, with sulfur no. 6. Same treatment as in 1938.
Curves 3, 4, field test, in 1940; four thorough mixings, and let stand overnight.

        B, Effect of linseed oil on the percentage of sulfur burned:

Curve 1, laboratory test, in 1938, with sulfur no. 1.
Curve 2, laboratory test, in 1940, with sulfur no 6. Same treatment as in 1938.
Curves 3, 4, field test, in 1940; four thorough mixings, and let stand overnight.

of sulfur when added in finely divided amounts up to 0.07 gram. News-paper scraps, sawdust, and burlap lowered the percentage of sulfur burned very little when present in amounts less than 0.03 gram; but in larger amounts, up to 0.07 gram, they reduced the amount of sulfur burned to about one half. Since sugar had practically no effect on the burning of sulfur, its curve is not given in the figure.

Figure 4 shows the effect of stearic acid, oleic acid, turpentine, and gasoline in unmixed and thoroughly mixed samples. The unsaturated acid, oleic, shows the largest reduction in the amount of sulfur burned. The test with gasoline affected the burning of sulfur very little, prob-ably because of its high volatility.

Field Experiments.—The laboratory experiments furnished striking data on the deleterious effect of small amounts of certain carbon and carbonaceous material on the burning qualities of sulfur. The next step in this work was to learn how data obtained under laboratory conditions checked with those secured under field conditions, where large quantities of sulfur (4 or more pounds) are burned in commercial sulfuring houses. Accordingly a three-compartment sulfuring house[7] on the Davis campus
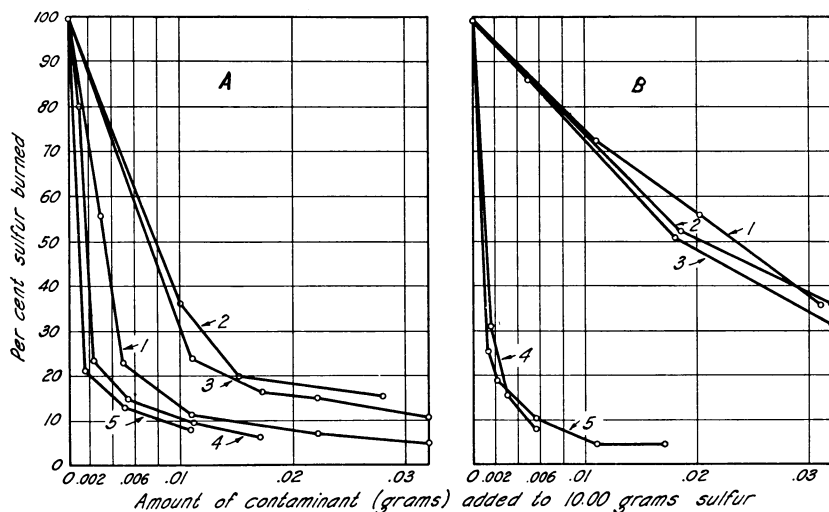

Fig. 6.—*A*, Effect of lubricating oil on the percentage of sulfur burned:
Curve 1, laboratory test, in 1938, with sulfur no. 1.
Curves 2, 3, laboratory test, in 1940, with sulfur no. 6. Same treatment as in 1938.
Curves 4, 5, field test, in 1940; four thorough mixings, and let stand overnight.

　　　　　B, Effect of turpentine on the percentage of sulfur burned:
Curve 1, laboratory test, in 1938, with sulfur no. 1.
Curves 2, 3, laboratory test, in 1940, with sulfur no. 6. Same treatment as in 1938.
Curves 4, 5, field test, in 1940; four thorough mixings, and let stand overnight.

was used for these tests. A high-grade sulfur (no. 6), which burned 99.75 per cent, was used as a base to which were added varying amounts of lubricating oil, fuel oil, linseed oil, turpentine, newspaper, sawdust, and burlap sacking. Since in the 1938 laboratory work sulfur no. 1 was used, some laboratory tests on sulfur no. 6 were made for comparison. The amount of sulfur used in each of the field trials was 1,800 grams (nearly 4 pounds). These samples were burned in clean metal pans in an empty sulfuring compartment.

To facilitate comparison between the laboratory and field results, the

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[7] This sulfuring house was constructed according to the design by Long, Catlin, and Nichols, given in California Agricultural Extension Service Farm Building Plan C–173. 1934.

latter data were recalculated to fit the scale used in the graphs of the 1938 laboratory experiments. Figures 5 to 7 show the data in this form.

The effect of contaminants on burning were on the whole greater in the field than in the laboratory. As figure 5, *A*, shows, approximately a
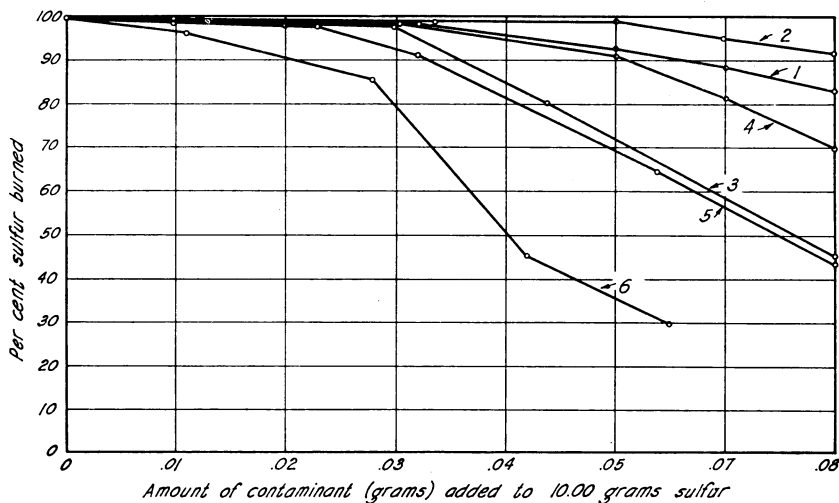

Fig. 7.—Effect of burlap sacking, newspaper, and sawdust on the percentage of sulfur burned:

Curve 1, burlap sacking added. Laboratory test, in 1938, with sulfur no. 1.
Curve 2, burlap sacking added. Field test, in 1940, with sulfur no. 6.
Curve 3, newspaper cuttings added. Laboratory test, in 1938, with sulfur no. 1.
Curve 4, newspaper cuttings added. Field test, in 1940, with sulfur no. 6.
Curve 5, sawdust added. Laboratory test, in 1938, with sulfur no. 1.
Curve 6, sawdust added. Field test, in 1940, with sulfur no. 6.

50 per cent reduction in the burning of sulfur was caused by 0.01 gram fuel oil in the laboratory tests, whereas in the field only 0.0014 gram (one seventh as much) was needed to produce the same reduction. In figure 5, *B*, 0.016 gram linseed oil lowered burning to about 30 per cent in the laboratory, while in the field 0.0052 gram reduced the burning to 24–29 per cent in two series of trials. Still more striking were the tests with turpentine in figure 6, *B*. With 0.02 gram turpentine in the laboratory, sulfur burned approximately 55 per cent; but in the field only 0.001 gram (one twentieth as much) was needed to bring about a similar reduction. Lubricating oil in figure 6, *A*, does not show so great a difference between the 1938 laboratory tests and the 1940 field results. With 0.0048 gram lubricating oil, sulfur burned 22.5 per cent in the laboratory; and in the field 0.0014 gram produced the same result. The curves obtained in the 1938 and the 1940 laboratory tests for lubricating oil do not check as they do for fuel oil, linseed oil, and turpentine. This dif-

ference may be caused by a somewhat different grade of lubricating oil used in 1940. If the 1940 data are used for comparison, the difference between laboratory and field results is greatly increased.

In figure 7, sawdust in the field experiments reduced the burning of sulfur much more than it did in the laboratory. This is not the case with newspaper cuttings and burlap sacking, whose field curves lie above those of the laboratory. No satisfactory explanation was found for this reversal.

In the field the sulfur is burned in an enclosed chamber where the air intake is greatly reduced and the sulfur dioxide gas accumulates to a large extent, whereas in the laboratory the sulfur is burned in the open with free access to air and with no accumulation of gases. This difference in burning conditions perhaps explains the greater reduction of contaminated sulfur burned in the field experiments.

Sources of Contamination.—As for the sources of contamination of sulfurs in actual practice, the contaminants may be matches, rags, or papers dropped carelessly into the sulfur after igniting it; from admixture with impure slag in the burners from pervious burnings; from oily floors on which the sacks of sulfur may have been stored; or from burlap sacks containing some oily matter. In the two last-mentioned instances such contaminating materials will penetrate the sulfur in the sacks by diffusion and reduce the percentage of sulfur that will burn freely.

Experiments (made in 1938) in which samples of sulfur no. 1 were placed in the vapors arising from the surface of heavy diesel fuel oil held at room temperature (25° C or 77° F) showed, in every case, a noticeable increase in black film formation and a decrease in the percentage of sulfur burned when compared with that of the original sulfur sample. One sample stored for 6 days over the fuel oil showed a decrease of 9 per cent in the percentage of sulfur burned. These results indicate that the oil vapor is absorbed by the sulfur at ordinary temperatures.

Another source of contamination may go back to the origin and preparation of the sulfur. In the preparation, traces of hydrocarbon oils may be introduced from pipes used to convey steam and from contamination by traces of oil from contiguous strata. Several fractional distillations[8] are required to remove the last traces of hydrocarbons from sulfur during preparation or refining.

This investigation did not aim to determine whether the carbonaceous matter in poor-burning commercial sulfurs is caused by insufficient refining, subsequent contamination, or both.

Purification of Contaminated Sulfur.—A method for freeing sulfur from interfering contaminants consists in heating the crude sulfur under

[8] See page 19 of citation given in footnote 6.

pressure over a temperature range of 255° to 320° C for a sufficient period to complete the chemical reactions. The excess sulfur is then sublimed from the residue.

Tests were made with solvents to ascertain whether contaminating materials could be removed by extraction. As table 1 shows, the solvent action of ethyl ether was somewhat better than that of petroleum ether on the impurities in the sulfur. Commercial sulfur no. 4 normally burned 39.0 per cent; but when extracted with petroleum ether it burned 83.7 per cent, and with ethyl ether, 89.5 per cent. The next greatest effect was with no. 5, which burned 61.0, 82.4, and 91.2 per cent, respectively.

TABLE 1

PERCENTAGE OF SULFUR BURNED BEFORE AND AFTER THREE-HOUR
EXTRACTION OF TEN-GRAM SAMPLES WITH SOLVENTS

Sulfur no.	Before extraction	After extraction	
		With petroleum ether	With ethyl ether
2	74.0	84.5	90.5
3	70.0	91.0	92.2
4	39.0	83.7	89.5
5	61.0	82.4	91.5

Extractions with methylene chloride and ethylene chloride were not successful; 20 to 25 per cent of the sulfur dissolved, and difficulty was also experienced in removing the last traces of the solvents from the undissolved sulfur.

Extraction of poor-burning sulfurs with petroleum and ethyl ethers increased the percentage of sulfur burned up to 90 per cent or above; but the volatility and inflammability of these solvents and the difficulty of their complete removal from the treated sulfur makes this treatment non-feasible for growers as a means of purifying sulfur.

Effect of High Temperature on Poor-burning Sulfurs.—Another method of increasing the burning quality of low-grade sulfurs has more promise. As stated before, scum formation decreases the burning area, lowers the temperature of the molten sulfur, and causes the flame to die out. To study the effect of maintaining the temperatures of the dishes containing the burning sulfur at higher levels, samples of medium-burning and poor-burning commercial sulfurs were placed in a sandbath; and the bath was heated to 300° C (572° F) and maintained at that temperature after igniting the sulfurs. The results are given in table 2. In all cases the percentage burned was increased. Judging from these tests, if the temperature of the pans containing poor-burning sulfurs can be

maintained at about 200° C, these sulfurs will burn almost completely. Even at 150° C sulfurs nos. 2 and 3 burned 98.1 and 99.6 per cent (table 2). Preventing or minimizing the loss of heat from the pans is definitely indicated. Some growers have placed asbestos or other insulating material around the sulfur pans, and thereby obtained some measure of success in increasing the amount of sulfur burned. Application of heat

TABLE 2

EFFECT OF RAISING TEMPERATURE OF SULFUR ON PERCENTAGE BURNED

Sulfur no.	Room temperature 25°–30° C	Sandbath maintained at		
		300° C	200° C	150° C
2.....................	74.0	99.9	99.6	99.6
3.....................	70.0	99.9	99.7	98.1
7.....................	34.8	99.9	99.6	96.2
8.....................	34.0	99.9	99.7	96.5

to the sulfur containers by a regenerative heating process holds some promise of usefulness, but this process requires careful control of the amount of air used to burn the sulfur completely.

SUMMARY

As chemical tests showed, the black film consisted almost entirely of carbon or carbonaceous material, with small amounts of siliceous matter and iron compounds.

Small amounts of inorganic materials such as dust and iron oxide have practically no effect on reducing the percentage of sulfur burned.

Judging from experiments on black-film formation, carbon or carbonaceous matter originated most likely from the interaction of molten sulfur or hot sulfur vapors, with traces of certain organic impurities. Of the widely varying materials tested, the petroleum oils and turpentine produced the most pronounced effect on film production and also showed the greatest reduction of sulfur burned, whereas cellulose materials had the least effect.

Under field conditions the percentage of burning of contaminated sulfur was considerably less than in the laboratory. This decrease in combustibility was probably due to the limited access of air and the accumulation of sulfur dioxide in the sulfur chamber.

Extracting or washing poor-burning sulfurs with suitable solvents was found to increase the percentage of sulfur burned, but this method is not economical in farm practice.

Samples of sulfur stored 2 to 6 days in an atmosphere of vapors arising from fuel oil were found to absorb sufficient amounts of volatile carbon compounds to increase the black-film formation and decrease the amount of sulfur burned. This fact may be important in defining proper conditions for the storage of sulfur.

Raising the temperature of the sulfur container will almost completely burn a contaminated sulfur.