GAS MASKS FOR GASOLINE AND PETROLEUM VAPORS

BY

S. H. KATZ and J. J. BLOOMFIELD
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GAS MASKS FOR GASOLINE AND PETROLEUM VAPORS.\textsuperscript{1}

By S. H. Katz and J. J. Bloomfield.

INTRODUCTION.

Vapors of petroleum, gasoline, and other products of petroleum—all of which are termed petroleum vapors in this paper—cause anesthetic effects when inhaled. "Gasoline jags" are frequent among workers in oil refineries, dry-cleaning establishments, rubber factories, and other plants using gasoline. Occasionally men are overcome,\textsuperscript{2} and some have died in consequence of breathing the vapors.\textsuperscript{3} Aside from the hydrocarbon vapors themselves, some petroleums such as Mexican and that from the Ohio field contain in solution, and evolve when exposed, hydrogen sulphide gas, which is exceedingly poisonous when breathed, quickly causing unconsciousness and death.

Men sometimes have to enter tanks, tank cars, bunkers of ships, or other containers that hold vapors of gasoline or petroleum, in order to make inspections, repairs, or adjustments. Of course, it is best when the work is extensive to clean and ventilate the space thoroughly in order to insure a supply of pure air before workmen enter; but sometimes this is not feasible or is inordinately expensive when the job is small. Under such circumstances the gas mask, the hose mask, or the self-contained oxygen breathing apparatus may give adequate protection for completing a job with a minimum of time, labor, and expense. When tanks are cleaned it is sometimes necessary to enter them before the vapors are wholly eliminated; a little protection then will usually enable men to work in comfort, whereas otherwise the vapors may be very annoying even if not especially dangerous. Small respiratory apparatus, such as the gas mask, is often helpful to factory workers who encounter similar vapors.

This paper gives the results of work on the degree of protection afforded by the canister type of gas mask, the hose mask, and the self-contained oxygen breathing apparatus against gasoline vapors.

\textsuperscript{1} Submitted by S. H. Katz to the faculty of the University of Pittsburgh by the senior author as partial requirement for the degree of chemical engineer. Suggestions and encouragement from Prof. H. C. Bashloum are gratefully acknowledged.

\textsuperscript{2} New York Times, Six, loading gasoline, overcome by fumes: Vol. 70, Aug. 5, 1921, p. 4, col. 6.

and the like. In general, the gas mask with canisters containing fresh, dry, activated charcoal gives protection for a limited time against hydrocarbon vapors in concentrations not exceeding 5 per cent in air. Higher concentrations may quickly penetrate a canister. The hose mask gives good protection against all concentrations that a man’s skin will bear. The thin rubberized bags of the self-contained oxygen breathing apparatus can be penetrated by gasoline vapors, but bags of rubber one-sixteenth inch thick exclude them.\footnote{Fieldner, A. C., Katz, S. H., and Kinney, S. P., Permeation of oxygen breathing apparatus by gases and vapors: Tech. Paper 272, Bureau of Mines, 1921, 24 pp.}

**ACKNOWLEDGMENT.**

This work was done under the general direction of A. C. Fieldner, superintendent and supervising chemist of the Pittsburgh experiment station, and R. R. Sayers, chief surgeon, Bureau of Mines. The earlier work was conducted by the Bureau of Mines independently but later with the cooperation of the American Petroleum Institute through its director, Dr. Van. H. Manning.

The following members of the Atlantic Refining Co., Philadelphia, Pa.: E. C. Esterly, constructing engineer; F. G. Delbridge, chief chemist; Charles Brown, safety engineer; and M. J. Welsh, foreman; and also members of the Gulf Refining Co., Pittsburgh, Pa.: C. H. Dugal, manager of Ben Venue station, and William Westenberger, jr., assistant manager, gave generously of their time and information and assisted the authors in conducting tests at the plants. Many other members of the American Petroleum Institute supplied information on their methods of using and experiences with respiratory apparatus.

G. W. Jones and W. P. Yant, assistant chemists, Bureau of Mines, analyzed the gases and vapors sampled in the course of this work. N. A. C. Smith, petroleum chemist, and W. A. Jacobs, chemical engineer, of the petroleum division, Bureau of Mines, were consulted freely.

The authors gratefully acknowledge constructive criticism and suggestions from the persons mentioned and others.

**GAS MASKS WITH ACTIVATED CHARCOAL ADSORBENT.**

The canister-type gas mask, the type commonly known since the World War, is now widely used for protection against many gases and vapors encountered in civil life. This mask, as used for military purposes, has inherent limitations in industry, in that it does not completely restrain and absorb gases exceeding 2 to 5 per cent in air; it becomes saturated after a certain amount of gas or vapor is taken up; it does not absorb ammonia gas or carbon monoxide; and
it does not supply oxygen which is needed to support life in atmospheres deficient in oxygen. The Bureau of Mines called attention to these deficiencies as soon as the mask was taken up for civilian purposes. Since then the bureau has developed the “universal” gas mask that protects against ammonia, carbon monoxide, and all other poisonous gases; but the limitations regarding high concentrations of gas and inability to supply oxygen still hold for all canister gas masks.

The canister of the Army mask contains a granular mixture of soda lime and activated charcoal. Soda lime is especially useful for absorbing acid gases, such as hydrogen sulphide, sulphur dioxide, phosgene, chlorine, and many others. It has no value whatever against organic vapors, which include gasoline and petroleum vapors, benzene, aniline, chloropicrin, and the like; activated charcoal absorbs (more correctly, adsorbs) these. Hence, when a mask is intended for use solely against a vapor such as gasoline, it gives longer life and better service if filled with charcoal only. The ability of charcoal to adsorb gasoline vapor has led to its use in extracting gasoline from natural gas; its action there is entirely similar to its action in removing gasoline from air breathed through a canister. Because a certain quantity of charcoal can take up only a limited amount of gasoline at a limited rate, a gas mask will allow vapors to penetrate after the charcoal becomes saturated or when the vapor concentration exceeds the activity of the charcoal to restrain and adsorb it.

**ACTIVATED CHARCOAL.**

Ordinary charcoal made by destructive distillation of wood has the property of adsorbing very small amounts of gas and vapor. Since adsorbents of maximum adsorbing property were needed for gas masks during the war, experiments led eventually to the large-scale production of “activated” charcoal. Coconut shells were first destructively distilled at temperatures up to 1,000° C. and then “activated” by superficially oxidizing them with air or steam to remove from the surfaces of the carbon structure “stabilized hydrocarbons” or “inactive carbon” deposited by the decomposition

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of hydrocarbons at high temperatures. The residue of "activated carbon" has an enormously increased capacity for adsorption. Activated charcoal has been shown to contain within its structure innumerable submicroscopic capillaries and pore spaces ranging in mean diameter between $2.8 \times 10^{-7}$ and $9.2 \times 10^{-7}$ cm., with $1.3 \times 10^{-6}$ cm. as maximum; and the surfaces exposed in these minute openings (160 to 436 square meters per gram) are enormously great compared to the external surfaces.

Molecules of gas or vapor that encounter these surfaces are held fast (adsorbed) in layers one to several molecules thick, and in some circumstances capillary action, as exhibited by liquids, plays a part. The forces that hold the adsorbed molecules to those of the charcoal are of the same nature as those that bind together the molecules of solids and liquids or the atoms of chemical compounds.

Charcoal eventually becomes saturated with gas or vapor; that is, equilibrium between the adsorbed phase held by capillarity and the gaseous phase ensues, and thereafter adsorption proceeds no further. The equilibrium is disturbed when the partial pressure of the gaseous constituent, or the temperature, changes. Thus at higher partial pressures a charcoal adsorbs more; then, if the partial pressure of the gaseous constituent is lowered, some of the adsorbed gas is emitted. Similarly, at lower temperatures more gas is adsorbed, and adsorbed gases are evolved when the charcoal is heated. As a general rule the lower the temperature of a vapor compared to its boiling point the more readily is the vapor adsorbed by charcoal.

**GASOLINE AND PETROLEUM VAPORS.**

Gasoline consists of a mixture of the lighter and more volatile hydrocarbon liquids that constitute petroleum. The main components of gasoline belong to the paraffin series ($C_nH_{2n+2}$) and may range from butane ($C_4H_{10}$) to nonane ($C_9H_{20}$), although dissolved hydrocarbon gases, air gases, some unsaturated compounds, and cyclic compounds may be present. The lighter compounds have higher vapor pressures, volatilize more readily, and hence tend to mix in larger proportion with air. Kerosene is that fraction of petroluem which distills at temperatures just above those of the gasoline fractions; after kerosene come gas oil and the lubricating oils. Kerosene and the heavier fractions are so much less volatile than gasoline at ordinary temperatures that the danger from breathing them is of minor importance.

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Petroleums are mixtures of numerous hydrocarbons whose molecular weights range from light to heavy. Refining simply separates this mixture of hydrocarbons into simpler parts and removes small amounts of impurities. Petroleums usually contain more dissolved gases—including the natural-gas paraffins (methane, ethane, and propane), air, and carbon dioxide, which in themselves are not poisonous—than refined products, but some petroleums contain hydrogen sulphide, which is exceedingly poisonous. Most petroleums present the same respiratory hazards and problems as gasoline and the other light products obtained by refining.

**PHYSIOLOGIC EFFECTS OF PETROLEUM VAPORS.**

Inhalation of gasoline and other volatile hydrocarbons given off by petroleum causes headache, dizziness, and frequently an intoxication in which the victim becomes excited and hysterical. Experiments made by the Bureau of Mines have shown that the odor of gasoline is noticeable in inhaled air containing 0.03 per cent gasoline; in air containing 0.07 increasing to 0.28 per cent gasoline a man became dizzy at the end of 14½ minutes; in a concentration of 1.13 to 2.22 per cent for three minutes a man became so dizzy that he was compelled to hold fast to a table to be able to stand; in a concentration increasing from 2.22 to 2.60 per cent, a man became dizzy after only 10 to 12 breaths. Lehmann gives 15 to 25 mg. of gasoline to a liter of air, corresponding to 0.13 to 0.71 per cent, as the maximum that can be inhaled within 30 minutes to one hour without causing serious disturbances. More recently Haggard showed that, when concentrations were gradually increased from zero, dogs exhibited each of the various physiological symptoms at practically the same concentrations, although the time factor varied somewhat. Thus, in several experiments in which dogs were placed in pure air to which gasoline vapor was added gradually, convulsions always occurred when 1 per cent concentration of gasoline vapor was attained, although the periods of exposure varied from 12 to 35 minutes; this was followed by immobility when the concentration reached 1.6 per cent after total exposures of 16 to 44 minutes. One of the tests was carried further; anesthesia resulted after a total exposure of 28 minutes, at which time the concentration was 2.3 per cent. Four minutes later this dog died. The final concentration was 2.6 per cent.

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The stage between unconsciousness and death is thus very narrow, making the vapors of the higher hydrocarbons dangerous anesthetics. High concentrations of the vapors quickly overcome the victims, causing complete insensibility and then death. However, when a victim still living is removed to fresh air, he usually recovers. The Schaef er¹³ prone pressure method of artificial respiration should be used to resuscitate if breathing is shallow or has ceased. Recovery is sometimes accompanied by severe headache and sometimes by nausea.

TESTS OF GAS MASKS AGAINST GASOLINE VAPORS.

Gas masks were investigated for completeness and duration of protection against gasoline vapors. Tests were made with chemical testing machines and by men wearing the masks in atmospheres containing the vapors. In the tests three classes of gasoline were used—very light casing-head gasoline, and high-grade and low-grade motor gasoline. The gasoline vapors present the greatest hazards and the conditions that make protection most difficult; tests against other types of vapor were not made, since masks will provide equal or greater protection against other petroleum products.

DESCRIPTION OF GAS MASKS.

Plate I, A, shows a United States Army Tissot-type gas mask, which in all essentials has been generally adopted for industrial use. The face piece, fashioned of stockinet-covered rubber one-sixteenth-inch thick, forms a pocket over the face and allows breathing through the nose. A corrugated, noncollapsible rubber tube connects the face piece with the canister, which is supported in a haversack hung from the neck and held against the chest by a cord around the body. Inhaled air enters through the bottom of the canister, is purified there, and passes to the face piece. The eyeglasses are of nonshatterable glass, large enough to allow a wide angle of vision; they are kept free of fog by the dry incoming air delivered against them. Exhaled air escapes through a "flutter" valve. The elastic head harness may be adjusted to size. This mask is a later development and is much more comfortable than the R. F. K. type with mouthpiece and nose clips which was worn during the war.

The same Tissot face piece is used with canisters of different sizes, containing different adsorbents. In the tests described hereinafter, canisters holding about 1 ¼ pints or 600 c. c., 1,500 c. c., and 3,600 c. c., respectively, of activated charcoal or soda lime were employed. Plate I, B, represents a mask with the large 3,600 c. c. canister supported and held by straps around the neck and the body. Figures 1 and 2 give details of the 600 c. c. and the 3,600 c. c. charcoal-filled canisters. The 1,500 c. c. canister has dimensions of

A. UNITED STATES ARMY TYPE GAS MASK WITH KOPPS-TISSOT FACE PIECE; CANISTER HOLDS 600 C. C. OF ADSORBENT AND IS SUPPORTED IN HAVERSACK HUNG FROM WEARER'S NECK

B. GAS MASK WITH LARGE CANISTER HOLDING 3,600 C. C. OF CHARCOAL HAS GREATER CAPACITY FOR GASOLINE VAPORS, AND GIVES LONGER TIME OF PROTECTION
Figure 1.—Small canister, holding 600 c.c. of granular activated charcoal.
Figure 2.—Large canister, holding 3,600 c.c. of granular activated charcoal.
Apparatus for Testing Canisters Against Gasoline Vapors
APPARATUS FOR TESTING CANISTERS AGAINST GASOLINE VAPORS, WITHOUT THE GAS INTERFEROMETER
2\(\frac{3}{8}\)\(\times\)6\(\frac{3}{4}\)\(\times\)7 cubic inches, otherwise it is similar to the 3,600 c. c. size.

Adsorbents in the canisters are granular, sized between screens of 8 and 14 meshes per inch. In the 600-c. c. canister, the adsorbent is divided into three portions of 200 c. c. each by filters of cotton wool which arrest mists, smoke, dust, or other suspensions that otherwise are not removed. At the top of the charcoal is a filter of turkish toweling and a stiff screen which holds the granules in place through the pressure of a strong spring. The 1,500 and 3,600 c. c. canisters have two cotton-wool filters, one of which is at the top. The canister cases of tin plate are identical in design to the canister of the United States Army gas mask used during the World War, and need no special explanation. These three types of masks weigh 4, 5\(\frac{1}{4}\), and 8 pounds, respectively, and are much lighter than other types of breathing apparatus.

TESTING MACHINE.

A diagram of the apparatus for testing canisters against gasoline vapors is given in Plate II. Plate III shows the apparatus without the gas interferometer.

The method of testing is the same in principle as used against various gases and vapors during the World War—that is, air mixed with 1 per cent of gasoline vapor is blown through the canister at the rate of 32 liters per minute, and the time during which all gasoline is retained by the canister is taken as the measure or life of the canister.

As Plate II shows, the air first bubbles through bottles containing sulphuric acid solution to maintain a 50 per cent relative humidity, because moisture changes affect the charcoal. The air then passes to an orifice connected by tubes to a constant-flow device, which automatically causes 32 liters per minute to pass to the canister, regardless of any changes in canister resistance. A mechanism then puts liquid gasoline into the air line, where the gasoline vaporizes.

This mechanism was devised for especial use with gasoline, because constancy of gasoline-vapor output, unlike that of the water vapor mentioned above, can not be controlled by simple means. A pure liquid consisting of a single component has a definite vapor pressure at any one temperature, and can saturate air passed

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through it to definite and uniform concentrations. Control of the
temperature gives control of the concentrations.

Gasoline is a mixture of various liquid hydrocarbons; it tends first
to evolve more of its lighter and more volatile constituents, leaving
a liquid of decreasing volatility; the constituents of the vapor change,
and the vapor concentration decreases progressively. The mechanici-
cal method of adding gasoline continuously and in measured flow to
the air stream and then volatilizing the gasoline completely has
given good results in canister testing. The mechanism consists of a
constant-speed motor which is geared through a series of reducers
and step pulleys to a screw that raises a mercury-leveling bottle at a
constant rate. Liquid gasoline in a burette is displaced by the mer-
cury and flows into the air line; to assist its vaporization the gasoline
is heated at this point by means of an electric tube furnace.

The air and vapor pass through a mixing bottle, and then through
the canister; or they may be by-passed around the canister and
escape through an outlet tube. Concentration of the vapors is de-
termined by drawing a small portion of the gases through an inter-
erometer, with which air-gasoline mixtures are quickly analyzed.
Gases entering the interferometer are dried with fused calcium
chloride to eliminate the effects of moisture. Before use, the inter-
erometer is calibrated empirically against various concentrations in
air of the vapors of each gasoline, by comparison with analyses by
the Haldane apparatus.18

GASOLINES USED.

Three gasolines used in the tests were: (1) Very light casing-head
gasoline; (2) a high-grade motor gasoline made by the straight dis-
tillation of Pennsylvania crude oil, nominally 68° to 70° B.; and (3)
a low-grade motor gasoline made by cracking. Table 1 gives analy-
ses and the average molecular weights as determined by the Victor
Meyer method.

17 Selbert, F. M., and Harpster, W. C., Use of the interferometer in gas analysis: Tech.
### Table 1—Molecular weights and analyses of gasolines.

<table>
<thead>
<tr>
<th>Kind of gasoline</th>
<th>Casing head</th>
<th>65° to 70° B. distillate from Pennsylvania crude</th>
<th>Motor gasoline from cracking process</th>
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<tbody>
<tr>
<td>Original gasoline</td>
<td>80</td>
<td>110</td>
<td>120</td>
</tr>
<tr>
<td>Nonvolatile residue from tests</td>
<td>160</td>
<td>166</td>
<td>106</td>
</tr>
<tr>
<td>Volatilized fractions in tests</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Specific gravity (15° C.)</td>
<td>0.8685</td>
<td>0.7150</td>
<td>0.7440</td>
</tr>
<tr>
<td>Degrees Baume</td>
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<td>65.8</td>
<td>58.2</td>
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<tr>
<td>Color</td>
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<td>Water white</td>
<td>Slightly yellow</td>
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<tr>
<td>Odor</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Acidity</td>
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<td>Negative</td>
<td>Negative</td>
</tr>
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<td>Doctor test</td>
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<td>Negative</td>
</tr>
<tr>
<td>Unsaturation</td>
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<th>Barometer, 747 mm.; temperature, ° C.</th>
<th>Barometer, 747 mm.; temperature, ° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount distilled:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First drop</td>
<td>33</td>
<td>45</td>
<td>46</td>
</tr>
<tr>
<td>5 per cent</td>
<td>37</td>
<td>56</td>
<td>60</td>
</tr>
<tr>
<td>10 per cent</td>
<td>40</td>
<td>64</td>
<td>68</td>
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<tr>
<td>20 per cent</td>
<td>45</td>
<td>76</td>
<td>82</td>
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<td>30 per cent</td>
<td>49</td>
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<td>50 per cent</td>
<td>59</td>
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<td>128</td>
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<td>70 per cent</td>
<td>71</td>
<td>142</td>
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<tr>
<td>80 per cent</td>
<td>80</td>
<td>160</td>
<td>166</td>
</tr>
<tr>
<td>90 per cent</td>
<td>97</td>
<td>181</td>
<td>185</td>
</tr>
<tr>
<td>95 per cent</td>
<td>125</td>
<td>204</td>
<td>215</td>
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<tr>
<td>Dry point</td>
<td>126</td>
<td>206</td>
<td>218</td>
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<tr>
<td>Distilled, per cent</td>
<td>96.0</td>
<td>96.5</td>
<td>95.0</td>
</tr>
<tr>
<td>Residue, per cent</td>
<td>0.5</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Loss, per cent</td>
<td>3.5</td>
<td>2.3</td>
<td>3.4</td>
</tr>
</tbody>
</table>

These gasolines present a range of high volatilities when compared with petroleum and its products in general; and having such properties, they are most likely to create high concentrations of vapors in air and also the conditions that are most hazardous with respect to the protection of men who might encounter them. The performance of canisters in restraining these vapors would be equaled or exceeded in giving protection against vapors of any other petroleum product, especially kerosene and the heavier distillates, because the vapor concentrations of those products are usually much less than the percentages used in the tests.
RESULTS OF MACHINE TESTS.

Tests have shown that the following factors influence the capacity of charcoal for adsorbing gasoline vapors: Nature and volume of the charcoal; moisture in the charcoal and in the air; kind of gasoline; concentration of gasoline in air; rate of air flow; and temperature. The temperature throughout the tests was normal—about 20°.

![Graph showing life of different sized charcoal canisters tested against casing-head gasoline. Charcoal, dry, 40-minute grade; relative humidity, 50 per cent; temperature, 25° C.](image)

Figure 2.—Graph showing life of different sized charcoal canisters tested against casing-head gasoline. Charcoal, dry, 40-minute grade; relative humidity, 50 per cent; temperature, 25° C.

to 25° C. (68° to 77° F.), which may be considered uniform; the relative humidity of the air was 50 per cent throughout. Other factors were varied, as is specified in the descriptions of the tests.

VOLUME OF CANISTERS AND CAPACITY FOR GASOLINE.

The life, under machine test, of canisters containing 600, 1,500, and 3,600 c. c. of dry activated charcoal, 40-minute grade by accelerated chloropicrin test, is shown in Figure 3. Casing-head gasoline was

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used in concentrations of 1 per cent (10,000 parts per million parts of air), 3 and 5 per cent; the rates of flow were 32 and 64 liters per minute. The life of canisters, the period during which they restrained all gasoline, is shown to be directly proportional to the amount of charcoal held.

**Effects of Moisture on Adsorption Capacity.**

The effect of moisture in charcoal was determined with small (600 c. c.) canisters manufactured in 1918. The charcoal in these canisters was 14-minute grade by accelerated chloropicrin test, much poorer than the good charcoal now on the market, which tests 40 minutes. Three moisture conditions were tried, as follows: (1) Air at room temperature was bubbled through water, thereby attaining 85 per cent relative humidity, and was passed through the canisters for six hours at a rate of 32 liters (1.13 cubic feet) per minute to permit moisture adsorption; (2) air-dry condition, the canisters having stood in ordinary room air for three years; and (3) dried, by drawing 32 liters of air per minute for four hours through the canisters in an oven heated to $105^\circ$ C. On a dry basis the moisture in the charcoal was found to be 21, 12, and 0.35 per cent, respectively.

Figure 4 shows results of representative tests of these canisters made by passing through them, at a rate of flow of 32 liters per minute, air containing 1 per cent of the casing-head, of the $68^\circ$ to $70^\circ$ B., or of the motor gasolines. The lower half of the figure compares the efficiencies (percentages of incoming gasoline vapor retained by the charcoal) with the duration of the test; in the upper part of the figure the efficiencies are plotted against the molecular volumes of the gasoline retained by the charcoal. As equal molecular volumes contain equal numbers of gasoline molecules, the upper curves indicate the relative numbers of molecules of each gasoline adsorbed.

The dry charcoal, indicated by $C$ in Figure 4, show 100 per cent efficiencies for 24 minutes against $68^\circ$ to $70^\circ$ B. gasoline, 25 minutes against motor gasoline, and 28 minutes against casing-head gasoline. These results seem irregular in view of the density and volatility of the gasolines; but the upper half of Figure 4 brings out greater regularity, indicating that the molecular volumes adsorbed are in reverse order to their volatilities. The inverted order is due no doubt to a tendency of the light casing-head gasoline to penetrate farther into the granules. As will be shown later, a penetration or "soaking-in" process renews the adsorptive capacity of used canisters.

The series for air-dry $B$ and humidified $A$ canisters show lives at 100 per cent efficiency of 11 to 14 minutes and of 2 to 4 minutes. No
regularity in respect to volatility of the gasolines and the molecular volumes adsorbed appears in the \( B \) and \( C \) series. The differences are not of much practical importance, since the lives are much less than those of the dry \( C \) canisters. The lack of regularity may be due in part to slight differences in moisture contents, irregular distribution of the moisture through the charcoal, or to errors of testing.

These tests show especially that canisters for petroleum vapors should be thoroughly dry, and should be guarded from moisture and humid air; the greater the moisture content the less is the residual capacity for gasoline. Canisters in equilibrium with 85 per cent humid air are almost useless.\(^{188}\)

In the foregoing tests the air used had a relative humidity of 50 per cent, which may be taken as an average condition. Such air, as compared with very dry air, would tend to shorten the life of canisters. Humid air gives up its moisture to dry charcoal, thus reducing the capacity of the charcoal to adsorb gasoline; on the other

\(^{188}\) Since the foregoing was written, an article by A. B. Ray, Industrial adsorption of gas and vapor with activated carbon; Met. and Chem. Eng., vol. 29, Aug. 27, 1923, pp. 345-349, says that wet activated carbon is "almost as effective an adsorbent for hydrocarbon vapors as is dried carbon." Such effects were not found in testing gas-mask canisters filled with activated coconut charcoal.
hand, humid air has less drying effect on canisters containing considerable moisture. Air with a moisture content greater than 50 per cent relative humidity tends still further to shorten the life of a canister. It is to be noted from Figure 4 that in all cases vapors penetrate canisters gradually, so that several minutes elapse before dangerous concentrations are passing. Since the odor of vapors in low concentrations is easily noticed, a person has ample time, after he detects vapors penetrating a gas mask, to return to fresh air before becoming incapacitated.

**METHOD OF CALCULATING MOLECULAR VOLUMES.**

In the tests against casing-head gasolines, all the liquid introduced into the air stream was volatilized and passed into the canister, but only a part of the 68° to 70° B. and the motor gasolines volatilized. Calculation of the molecular volumes of casing-head gasoline used is simple, as follows:

\[
\text{Molecular volumes} = \frac{\text{Volume of liquid} \times \text{density}}{\text{Molecular weight in grams}}.
\]

For 68° to 70° B. gasoline and motor gasoline, however, the average molecular weight of the evaporated fractions were unknown. The following example shows the calculations used to determine molecular volumes of the evaporated portions, the data being taken from a test with 68° to 70° B. gasoline:

**Density:**

- Original gasoline = 0.715  \(= d_0\)
- Residual gasoline = 0.752  \(= d_1\)
- Volatilized gasoline = (?) \(= d_2\)

**Molecular weight:**

- Original gasoline = 110  \(= m_0\)
- Residual gasoline = 160  \(= m_1\)
- Volatilized gasoline = (?) \(= m_2\)

**Volume of gasoline liquid:**

- C. c. delivered per minute = 1.87  \(= V_0\)
- C. c. residue per minute = 0.600  \(= V_1\)
- C. c. volatilized per minute \(^a\) = \(v_2 - v_1 = 1.27 = V_2\)

**Weight of gasoline:**

- Grams delivered per minute = 1.87 \(\times 0.715 = 1.337 = v_0 d_0 = w_0\)
- Grams residue per minute = 0.600 \(\times 0.752 = 0.451 = v_1 d_1 = w_1\)
- Grams volatilized per minute = \(w_2 - w_1 = 0.886 = v_2 d_2 = w_2\)

\[d_2 = w_2 ÷ v_2 = 0.886 ÷ 1.27 = 0.698\]

Molecular volume of perfect gas (25° C., 760 mm.) = 24.45 liters = \(V\)

Volume of \(w_0\) grams gasoline (25° C., 760 mm.) as perfect gas = \(V_0\)

Volume of \(w_1\) grams gasoline (25° C., 760 mm.) as perfect gas = \(V_1\)

Volume of \(w_2\) grams gasoline (25° C., 760 mm.) as perfect gas = \(V_2\)

\(^a\) Liquid gasoline fractions have constant partial volumes in gasoline mixtures.
GAS MASKS FOR GASOLINE AND PETROLEUM VAPORS.

Now,

\[ V_0 = V_1 + V_2 = V \times \frac{w_0}{m_0} \]

\[ V_1 = V \times \frac{w_1}{m_1} \]

\[ V_2 = V \times \frac{w_2}{m_2} \]

and,

\[ V_0 = V \left( \frac{w_1 + w_2}{m_1 + m_2} \right) = V \times \frac{w_0}{m_0} \]

Hence,

\[ \frac{w_0}{m_0} = \frac{w_1 + w_2}{m_1 + m_2} \]

\[ \frac{w_2}{m_2} = \frac{w_0}{m_0} - \frac{w_1}{m_1} \]

From which,

\[ m_2 = \frac{w_2 (m_0 m_1)}{w_0 m_1 - w_1 m_0} = \frac{(w_0 - w_1) m_0 m_1}{w_0 m_1 - w_1 m_0} \]

Substituting,

\[ m_2 = \frac{0.886 \times 110 \times 160}{(1.337 \times 160) - (0.451 \times 110)} = \frac{15590}{213.9 - 49.6} = 94.9 \]

Let molecular volume, in liquid form, of volatilized 68° to 70° B. gasoline = m

\[ m = \frac{m_2}{d_1} = 94.9 + 0.698 = 136. \text{ c. c.} \]

Fraction of molecular volume volatilized per minute = \[ \frac{v_1}{m} = \frac{1.27}{136} = 0.00934 \]

TESTS WITH HIGH CONCENTRATIONS OF GASOLINE VAPOR AND HIGH RATES OF FLOW.

The previous tests against 1 per cent of gasoline vapors in air show a relatively long life for canisters. If such concentrations were never exceeded in tanks and apparatus, there would be no hesitation in fully recommending the charcoal-filled canister gas masks; but 1 per cent concentrations are exceeded many times and adequate protection must be afforded by a gas mask whenever it is used.

Figure 5 gives results of tests with increasing concentrations of casing-head gasoline vapor at rates of flow of 32 and 64 liters per minute. The charcoal was dry and of 40-minute grade. The figure shows that the life of the charcoal is decreased by increasing concentrations in amounts more than inversely proportional to the concentrations. The same is true of the rate; thus a 600 c. c. size canister, tested at a rate of 32 liters per minute against 1 per cent vapor, lasted 62 minutes before beginning to fail; against 3 per cent vapor, 8 minutes; and against 5 per cent vapor, only 3\(\frac{1}{4}\) minutes. At a 64-liter rate, a 3,600 c. c. canister lasted 137 minutes against 1 per cent vapor, and 63\(\frac{3}{4}\) minutes against 5 per cent vapor. Under the latter conditions, a 600 c. c. canister would last only about 1 minute.
A robust man can breathe 64 liters per minute only for a very short time, and then only with utmost exertion. These tests show, however, what may be expected of canisters in an emergency. Five per cent of gasoline vapor may be taken as the limit in which a canister gas mask can afford protection, and these masks are not to be recommended for concentrations exceeding an average of 2 per cent.

A man on a new or unusual job often may not be aware of the concentration of the vapor, so safety demands that the concentrations be determined by chemical analysis to assure that a canister gas mask is adequate before the person's life is jeopardized. If a chemist...
is not available, or time for analysis is lacking, it is better to use a hose mask or self-contained oxygen breathing apparatus for protection. A generally safe rule to follow is to wear a canister gas mask for protection from petroleum vapors only when a man can work for a short time without respiratory protection.

At one refinery, at least, canister gas masks are now used by men working at the “rack” for filling tank cars. The cars, containing at times a little residual gasoline, arrive at the rack with the top manhole and the bottom drain pipes open. Before these tanks are filled, men enter and inspect them. Formerly the men used no respiratory protection, but held their breath or breathed as little as possible while in the vapors. Gas masks with charcoal-filled canisters of 600 c. c. size are now used continually on this job. Inspection of a car takes from one to three minutes, and canisters in service last several weeks before replacement. Conditions encountered in this service must be much less severe than those applied in the tests discussed above.

TESTS OF MASKS ON MEN.

Machine tests previously described give comparisons of the action of gas masks under various controlled conditions, but the final criterion must be their performance when worn by men.

Casing-head gasoline and 68° to 70° B. gasoline were put up in 1 per cent concentrations in the 1,000 cubic foot gas-chamber of the bureau at its Pittsburgh experiment station. Gas masks with 600-c. c. canisters containing air-dry (12 per cent moisture) activated charcoal, 14-minute grade by accelerated chloropicrin test, were worn in each vapor by two men—one large, weighing 210 pounds, and the other small, weighing 140 pounds. In the chamber they performed calisthenic exercises to accelerate breathing, which were alternated with periods of rest, and after exercising and resting for a total of 25 minutes completed the test by pumping air with a tire pump into a gas cylinder of about 1 cubic foot capacity.

During the 25 minutes of exercise and rest, the breathing ranged from approximately 8 liters per minute at the start to about 32 liters after acceleration by exercises. This latter figure is the breathing rate of a man doing ordinarily hard work or walking at a rate of 3½ miles per hour. Pumping air into the cylinder is severe exercise, and rapidly accelerates the breathing to a maximum rate of probably 50 to 60 liters per minute. In each test gasoline penetrated the canisters after about one minute of pumping, or about 26 minutes from the start of the test.

The canisters worn by the larger man “broke” first, but only by a fraction of a minute, because he breathed a greater volume of air.
Had the extra duty required in air pumping been omitted, the canisters would have undoubtedly lasted much longer. The 26-minute life of canisters worn by the men compares well with 11 minutes and 14 minutes by machine tests under similar conditions against 68° to 70° B. and casing-head gasolines, respectively. Thus in ordinary service and without excessive rates of breathing, a canister may last several times as long as indicated by machine tests under conditions otherwise similar.

**USED CANISTERS REVIVIFIED.**

All the tests described heretofore have been continuous; that is, gasoline vapors passed into a canister without interruption until it failed to adsorb and restrain them. It has been found, however, that the canisters tested beyond 100 per cent efficiency and then set aside for a time become revivified; they regain their capacity for gasoline vapor, and again show 100 per cent efficiency, but for a shorter time, when tested. Similarly, canisters tested intermittently without being forced to their “break” show a longer summation of test life than in continuous tests.

For instance, a canister of these specifications—600 c. c. of activated charcoal, 14-minute grade by accelerated chloropicrin test, and air-dry—was tested by machine against 1 per cent of casinghead gasoline in air, until, after 20 minutes, it retained only 57 per cent of the incoming vapor. The canister then stood in laboratory air for 52 days; it was neither stoppered nor protected in any way and possibly some adsorbed gasoline may have escaped; however, no gasoline vapor could be detected when later from time to time a man breathed through it. After 52 days the canister was replaced on the machine and tested further; it showed 100 per cent efficiency for 5 minutes, and it again showed 57 per cent efficiency after 14 minutes.

Another canister tested against motor gasoline gave 100 per cent efficiency for about 13 minutes; the test was continued until 50 per cent efficiency was recorded at 29 minutes, then the canister was set aside in the laboratory. Air breathed through the canister when set aside was heavy with gasoline vapors, but these gradually diminished until after a few days they were no longer perceptible. After 81 days the canister was tested again; it remained 100 per cent efficient for 2 minutes, then permitted a slow penetration of vapor, and reached 90 per cent after 18 minutes.

Such revivification of used canisters upon standing may be due partly to loss of gasoline by evaporation, but this is probably a minor influence, because canisters whose tests are interrupted for short periods (minutes) under conditions preventing evaporation often show increased total life. Moisture changes may also be accountable.
for some revivification. Tests do not show the absolute adsorptive capacity of charcoal, but rather the capacity for continuous adsorption under service conditions. More probably the increased life is due to a penetration, a soaking in or "drift" of the gasoline adsorbed on the outer surfaces of the charcoal granules, to the deeper parts, whereby the outer surfaces regain capacity. Canisters that are used intermittently in actual service thus give greater total life than those that are worn continuously in vapors to the limit of adsorptive capacity.

REVIVIFICATION WITH HEATED AIR.

As is well known, charcoal adsorbs more gases and vapors at lower temperatures and its adsorptive capacity decreases at higher temperatures. Hence, attempts were made to regenerate canisters by driving off the adsorbed gasoline with a current of heated air. Excellent results were obtained. Air at 100° C. drawn through at the rate of 1 cubic foot per minute regenerated the 600 c. c. canisters in two hours; tests for life nearly equaled the original or were greater when moisture in the charcoal was reduced simultaneously with the gasoline. A 3,600 c. c. canister regenerates similarly in 10 hours.

Canisters were used and regenerated repeatedly, an electric oven with automatic temperature control being employed for regeneration. The hot air was drawn through the canister in the oven and thence through a connecting pipe to a small motor-driven rotary pump outside. Care was taken to prevent gasoline vapors escaping into the oven itself, owing to the danger of explosion through ignition by electric sparks or hot parts. The temperature need not be maintained exactly at 100° C., but it must not exceed 150° C., because activated charcoal might take fire.

Laboratory equipment may not be available where gas masks are used, but suction can be improvised with steam or water-jet aspirators, and hot air or gases of proper temperature may be drawn from stacks or around furnaces or apparatus. The gases should be free from dust, smoke, and suspended matter. Steam can not be used, because it leaves moisture in the charcoal, greatly reducing the adsorbent capacity. Cotton-wool filters dampened by wet steam pack together in a canister and thus increase the resistance to breathing so much that the canister is useless.

The cost of regenerating charcoal-filled canisters is a fraction of the cost of new canisters, hence considerable saving may result from regeneration of gas masks used against petroleum vapors. Canisters containing a chemical adsorbent can not be regenerated.

HYDROGEN SULPHIDE GAS IN CRUDE OIL.

As previously stated, certain crude oils from the Lima field in Ohio, from Canada, and elsewhere, notably some from Mexico, contain hydrogen sulphide gas ($H_2S$) in solution, which is given off when the petroleum is heated or exposed to the air. Since $H_2S$ is much more poisonous than petroleum vapors, more pains should be taken to avoid it.

PHYSIOLOGICAL EFFECTS OF HYDROGEN SULPHIDE.

Hydrogen sulphide has an exceedingly disagreeable odor (like rotten eggs) when greatly diluted in air. At higher concentrations the odor disappears, due to anesthetic effect on the olfactory nerves; however, at concentrations above the odoriferous, a metallic taste persists that may be noticed by persons who are accustomed to the gas. Hydrogen sulphide is intensely poisonous and quickly causes unconsciousness and death because of its paralytic action on nerve centers controlling respiration and the heart. Sayers, Mitchell, and Yant found that 600 parts per million (0.06 per cent) of $H_2S$ in air renders a dog unconscious in about 2 minutes and kills it in about 15 minutes. Lehmann determined that persons were affected slightly after several hours’ exposure to concentrations of 100 to 150 parts per million, and that 1,000 to 2,000 parts per million are quickly fatal to men or animals. Its lack of odor in deadly concentrations makes hydrogen sulphide very treacherous. A number of men in the petroleum industry have died from inhaling it.

PROTECTION AFFORDED AGAINST HYDROGEN SULPHIDE BY CANISTERS.

Tests of canisters to determine the protection they afford against hydrogen sulphide were made with apparatus similar to that described previously, except that $H_2S$ was introduced into the air stream from a generator at a measured rate. The canisters contained activated charcoal, soda lime, or mixtures of soda lime and charcoal, respectively 40 and 60 per cent by volume. Some of the results are presented graphically in Figure 6, which shows the life of different size canisters, and Figure 7, which shows the variation in life against concentrations of $1/2$, 1, and 3 per cent of hydrogen sulphide in air. The tests were made at 32 liters per minute, at room temperature, and with 50 per cent relative humidity, corresponding to tests against gasoline vapor.

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21 Lehmann, K. B., Experimentelle Studien über den Einfluss technisch und hygienisch wichtiger Gase und Dämpfe auf den Organismus; Theil V. Schwefelwasserstoff: Arch. für Hygiene, Bd. 14, 1892, pp. 135–189.
The granular soda-lime adsorbent for acid gases, which include hydrogen sulphide, was prepared especially for use in gas masks according to the formula developed during the World War.\textsuperscript{21a} It contained hydrated lime, 45 parts; Portland cement, 14 parts; infusorial earth, 6 parts; sodium hydroxide, 1 part; water, 13 parts; and sodium permanganate, 2\(\frac{1}{2}\) parts. As shown by Figure 7, the canisters filled with soda lime restrain about four and one-half times as much hydrogen sulphide as those filled with dry, activated charcoal. However, soda lime has no capacity whatever for gasoline vapor. Moisture reduces the capacity of charcoal for gasoline but increases its capacity for hydrogen sulphide; for instance, a 600 c. c. canister of the charcoal equilibrated with air at 85 per cent relative humidity (21 per cent moisture on dry-charcoal basis) lasted 29 minutes against one-half of 1 per cent of \(\text{H}_2\text{S}\) (or almost as long as soda lime), as compared to three and one-half minutes for dry charcoal.

Figure 7 shows that the life of canisters containing soda lime is about inversely proportional to the concentration of \(\text{H}_2\text{S}\); a 600 c. c. canister lasted 34 minutes against one-half of 1 per cent and 6 minutes against 3 per cent. It is not feasible, however, to use gas masks in 3 per cent concentrations of hydrogen sulphide because of the intense heat produced by adsorption and by the neutralization of the alkali. Solder was melted on a 600 c. c. canister testing against 3 per cent \(\text{H}_2\text{S}\); and in a 1,500 c. c. canister the cotton-wool filters in the can were set on fire. When air with 3 per cent of \(\text{H}_2\text{S}\) was passed through a 1,500 c. c. canister of charcoal, the charcoal itself became ignited. The charcoal acts as a catalyzer, promoting the oxidation of \(\text{H}_2\text{S}\) by the air, with formation of sulphur dioxide and possibly sulphur trioxide and some free sulphur.\textsuperscript{22} The reactions seem to be—

\[
\text{2H}_2\text{S} + \text{O}_2 + \text{C} = 2\text{H}_2\text{O} + 2\text{S} + \text{C},
\]

\[
\text{2H}_2\text{S} + 2\text{O}_2 + \text{C} = 2\text{H}_2\text{O} + \text{SO}_2 + \text{C},
\]

\[
\text{H}_2\text{S} + 2\text{O}_2 + \text{C} = \text{H}_2\text{O} + \text{SO}_3 + \text{C}.
\]

Heat of this reaction is mainly responsible for ignition of the charcoal. At 3 per cent concentration of \(\text{H}_2\text{S}\) the gas that breaks through the charcoal is \(\text{SO}_2\), whereas at one-half and at 1 per cent it is \(\text{H}_2\text{S}\).

The charcoal curves in Figure 7 do not quite follow the inverse proportion; a little longer life is shown at higher concentrations than the inverse proportion requires. No doubt this is due to the charcoal adsorbing more tenaciously the sulphur or \(\text{SO}_2\) produced by the oxidation. Two points are plotted on Figure 7 showing the action of mixtures of dry activated charcoal (60 per cent by volume)


Figure 6.—Graph showing life of various sized canisters tested against 1 per cent hydrogen sulphide. Charcoal, 40-minute grade; rate of flow, 32 liters per minute; relative humidity, 50 per cent; temperature, 25° C.

Figure 7.—Graph showing effect of increasing concentrations of hydrogen sulphide on life of canisters. Charcoal, 40-minute grade; rate of flow, 32 liters per minute; relative humidity, 50 per cent; temperature, 25° C.
and soda lime (40 per cent by volume). The life determined for 600 c. c. canisters of the mixture is slightly higher than that which may be calculated on the basis of proportions of the two adsorbents. This increase is probably due to some moisture contained in the soda lime passing to the charcoal and increasing its capacity.

Based on these tests, gas masks can be recommended for use in concentrations of $\text{H}_2\text{S}$ in air averaging not over 1 per cent and not exceeding 2 per cent in irregular concentrations. The heat developed in canisters serves to indicate to the wearer the proportion of $\text{H}_2\text{S}$ encountered. On numerous occasions members of the Bureau of Mines have, with excellent results, used gas masks for protection from hydrogen sulphide during experimental work. The concentrations encountered in this manner, however, have not been high—0.3 per cent being the highest range.

**LIMITATIONS OF CANISTER GAS MASKS.**

Canister gas masks have special and important limitations that restrict their use to certain definite atmospheres. Below is a summary of the conditions in which canisters of activated charcoal and of soda lime are effective against petroleum vapors and hydrogen sulphide; but it must be remembered always that failure to conform to these conditions may jeopardize the wearer of a gas mask and even cause his death.

1. Canister gas masks containing up to 3,600 c. c. of activated charcoal do not protect against concentrations of petroleum vapors in air exceeding 5 per cent by volume, nor against concentrations of hydrogen sulphide exceeding 2 per cent.

2. The activity and capacity of these masks are insufficient to give practicable protection against concentrations continuously exceeding 2 per cent of petroleum vapors or 1 per cent of hydrogen sulphide on account of the short time of protection before vapors penetrate.

3. Canister masks containing only soda lime give no protection whatever against petroleum vapors; against hydrogen sulphide they give longer protection than charcoal, but they can be safely used only in concentrations that do not exceed 2 per cent.

4. Canister masks containing mixtures of activated charcoal and soda lime increase the protection against hydrogen sulphide over that afforded by an equal volume of charcoal alone but decrease the protection against petroleum vapors; similarly, the mixture, compared to soda lime only, affords protection against petroleum vapors but decreases protection against hydrogen sulphide.

5. Unless it is known from chemical analysis or other definite source that the vapors in question do not exceed the average concentrations stated above, canister gas masks must not be worn.
(6) Ammonia gas masks that contain copper sulphate impregnated on pumice granules (kupramite)\textsuperscript{23} as an ammonia absorbent, and other special gas masks on the market give no protection whatever against petroleum vapors and hydrogen sulphide.

(7) Canisters larger than 600 c. c. size give longer time of protection, but the average concentration stated above should not be exceeded.

**Hose Masks.**

The hose mask consists of a face mask or a mouthpiece attached to a long hose through which the wearer inhales fresh air. The length of hose limits the distance he may go from pure air into irrespirable gases and vapors. With three-fourths to 1 inch hose the distance may range up to 100 or 150 feet without causing undue exertion in drawing breath. Longer lengths of hose may require a pump or source of compressed air to force pure air to the wearer. The hose mask is not limited as regards the concentration or kind of irrespirable vapors or gas that surround the wearer; it protects against any atmosphere that the skin can endure. A number of forms of hose masks have been used for many years. Since the development of the Army gas mask the Tissot face piece attached to the hose has been most popular.

Three forms of hose masks made by the Bureau of Mines are shown in plates IV to V, C. Plate IV shows a Tissot-type face piece connected by flexible nonkinking rubber tube covered with stockinet to the long hose which is attached to a belt. In the union between the flexible tube and hose is a disc check valve to prevent passage of exhaled air into the tubing. The belt is of heavy cotton web 3 inches wide. The hose is solidly fixed to the belt at the front and side of the body with a strap between the hose and belt at the other side of the body dividing the drag. The hose is of rubber and cloth, three-fourths inch nominal inside diameter and 1\(\frac{1}{2}\) inches outside diameter; and an embedded stiff metal spiral prevents collapse. This hose is manufactured in 25-foot lengths, which may be joined when necessary. At the pure-air end of the hose there is a bell or funnel of wood and metal which raises the opening from the ground and helps to prevent the entrance of dust. A close-mesh screen in the funnel restrains coarse particles, and cotton wool or waste may be put into the funnel to prevent the entrance of finer dust. The hose should be blown out at intervals with compressed air to elimi-

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nate dust and sulphur which may bloom out on the rubber and irritate the wearer's eyes.

The hose mask in Plate V, A, is similar to the previous one, except that a McCaa harness is used instead of the belt. This harness is similar to that used with the McCaa oxygen breathing apparatus described later and is adjustable to various sizes. Plate V, B, shows a ring at the back between the shoulders providing for the attachment of a rope or life line to lift men from danger in emergencies. The hose is fastened to the harness high on the back. Two flexible rubber tubes lead from the face piece around both sides of the neck and connect through a T to the hose. This mask eliminates tubes in front of the body where they may interfere with work. No check valve was used, but the resistance to air flow through the hose was relied upon to cause exhalation through the flutter valve of the mask.

A hose mask similar to the preceding one, except that the face piece is replaced by a mouthpiece for breathing, is shown in Plate V, C. Plate V, B, shows the attachments on the back. The hose, harness, and attachments are identical with those in Plate V, A. The mouthpiece is similar to those used with self-contained oxygen breathing apparatus except that it is equipped with a flutter valve to eliminate exhaled air. Valves inside the metal tubes of the mouthpiece check any back flow of air. Straps fastening to a cap worn with this mask hold the mouthpiece in place. The nostrils are closed by a small clamp. Goggles to protect the eyes are necessary when this apparatus is worn in irritating gases, such as hydrogen sulphide and hydrocarbon vapors. This mask eliminates the discomfort of the face masks, especially in hot weather or in warm places.

Hose masks are simple, contain no chemicals nor parts that are easily used up, and require no replacements until worn out. There is practically no expense of upkeep, and there are no limitations as to the kind of atmosphere in which they give protection. Hose masks are especially useful around refineries, tanks, and apparatus for storing, handling, and shipping petroleum products and similar volatile liquids, because the wearer must penetrate relatively short distances from pure air.

AIR BLOWERS FOR HOSE MASKS.

Some hose masks are equipped with small hand-driven rotary blowers at the pure-air-end of the hose. Such a blower should be of a

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24 McCaa, George R., mine safety engineer, Pittsburgh experiment station, Bureau of Mines.

BUREAU OF MINES HOSE MASK WITH KOPPS-TISSOT FACE PIECE; THE HOSE IS STRONGLY FASTENED TO A WIDE, HEAVY WEB BELT
A. BUREAU OF MINES HOSE MASK WITH KOPPSTISSOT FACE PIECE ATTACHED TO THE McCAAA HARNESS

B. BACK VIEW OF HARNESS SHOWN IN PLATES V, A, AND V, C

C. BUREAU OF MINES HOSE MASK WITH MOUTHPIECE, ATTACHED TO THE McCAAA HARNESS; IT LEAVES FACE AND EYES UNCOVERED
type to force air with either direction of rotation and should cause no restriction to natural breathing by its failure to operate. Blowers are to be recommended because they exert positive pressure throughout a mask, and, should any leaks occur at joints or in the fit of the face piece, the leakage is outward—thus eliminating danger. Operation of the blower requires an attendant but this requirement increases safety; in fact, one or more attendants should always be at hand whenever a man enters an irrespirable atmosphere.

**LIFE LINES SHOULD BE USED.**

The Bureau of Mines recommends that a man entering a tank or other apparatus should always have a life line attached to his person and held outside by at least two strong men who can remove him in an emergency. Life lines are always expedient whether the respiratory apparatus be hose mask, canister gas mask, or self-contained oxygen breathing apparatus. If the harness is not arranged for attaching life lines, they can be tied around the waist.

**TESTS OF HOSE MASKS.**

Plate IV shows a hose mask with the hose attached to the belt. This mask was tested by the writers in gasoline storage tanks at a wholesale oil-distributing station. The tanks, 10 feet in diameter and 25 feet long horizontally, had been emptied except for a few inches of residual liquid. Entrance was gained through manholes at the top and down ladders. A rope held by two observers at the top was tied around the waist of the man, and the outside end of the hose was wired to a fixed rod to prevent its falling into the tank, the latter being a most important precaution under many circumstances.

Three grades of gasoline—absorption, straight-run, and naphtha—and one of kerosene (for distillation analyses see Table 2) were in the tanks. The outdoor temperature was 80° F., whereas that of the atmosphere and the liquids in the tank was 68° F. Table 3 gives analyses of samples of the tank atmospheres. The atmosphere in the tank containing absorption gasoline held over 90 per cent of hydrocarbon vapors and less than 2 per cent of oxygen—an atmosphere which would quickly overcome and kill an unprotected man. The tanks holding straight-run gasoline and naphtha also contained highly irrespirable atmospheres. The atmospheres in the kerosene tank would affect a man breathing it for some time.
### Table 2.—Distillation analyses of gasolines in tanks entered with hose masks.

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<tr>
<td>Specific gravity at 15° C.</td>
<td>0.727</td>
<td>0.661</td>
<td>0.756</td>
<td>0.802</td>
</tr>
<tr>
<td>Degrees Baumé</td>
<td>62.6</td>
<td>81.8</td>
<td>55.2</td>
<td>44.6</td>
</tr>
<tr>
<td>Barometer, 733 mm.; temperature, °C.—</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First drop</td>
<td>35</td>
<td>25</td>
<td>65</td>
<td>172</td>
</tr>
<tr>
<td>50 per cent</td>
<td>121</td>
<td>58</td>
<td>137</td>
<td>235</td>
</tr>
<tr>
<td>90 per cent</td>
<td>192</td>
<td></td>
<td>178</td>
<td>290</td>
</tr>
<tr>
<td>Dry point</td>
<td>221</td>
<td>157</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Distilled, per cent.</td>
<td>95.5</td>
<td>89.3</td>
<td>98.0</td>
<td>94.0</td>
</tr>
<tr>
<td>Residue, per cent.</td>
<td>1.0</td>
<td>1.6</td>
<td>1.1</td>
<td>4.4</td>
</tr>
<tr>
<td>Loss, per cent.</td>
<td>3.5</td>
<td>9.1</td>
<td>.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>

### Table 3.—Composition of atmospheres in tanks.

(Air temperature outside tanks, 80° F.; temperature of liquids and atmospheres in tanks, 68° F.)

<table>
<thead>
<tr>
<th>Tank No.</th>
<th>Sample No.</th>
<th>Kind of gasoline</th>
<th>Position of sample</th>
<th>Composition of atmospheres, per cent.</th>
<th>Hydrocarbon vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Straight-run</td>
<td>Top of tank</td>
<td>20.5</td>
<td>77.3</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>do.</td>
<td>4 feet above liquid</td>
<td>20.2</td>
<td>76.6</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>do.</td>
<td>6 inches above liquid</td>
<td>18.4</td>
<td>69.6</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>Absorption</td>
<td>Top of tank</td>
<td>9.0</td>
<td>34.1</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>do.</td>
<td>4 feet above liquid</td>
<td>1.8</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>do.</td>
<td>6 inches above liquid</td>
<td>1.4</td>
<td>5.2</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>Naphtha</td>
<td>Top of tank</td>
<td>20.0</td>
<td>74.6</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>Kerosene</td>
<td>do.</td>
<td>20.8</td>
<td>79.1</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>do.</td>
<td>Middle of tank</td>
<td>20.8</td>
<td>79.0</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>do.</td>
<td>3 feet above liquid</td>
<td>20.8</td>
<td>79.1</td>
</tr>
</tbody>
</table>

The man remained 10 minutes in tanks 1, 3, and 4 (Table 3), but he could remain in tank 2 only 6 minutes, as irritation of the skin caused by the highly concentrated vapors could be endured no longer, although no vapor was detected in the air he breathed. In other similar tests the masks have been worn by the writers for periods as long as half an hour, and might have been worn indefinitely so far as the protection was concerned.

Information given the Bureau of Mines by seven large oil-refining companies shows that the hose mask is most favored for protect-
BUREAU OF MINES HOSE MASK WITH KOPPS-TISSOT FACE PIECE; THE HOSE IS STRONGLY FASTENED TO A WIDE, HEAVY WEB BELT
Details of the McCAA Half-Hour Oxygen Breathing Apparatus

Circulation of air through apparatus: Oxygen from cylinder passes through closing valve into reducing valve, through metal tube inclined in cylinder, through admission valve to pressure gage, then through cooler to reduce the oxygen mixture with the inhalation air and passes upward through inhalation tube and valve into lungs, then back through exhalation valve and tube into the regulator, through reducing valve to cooler, and into breathing bag through exhalation tube and valve into lungs, and back through inhalation tube and valve into lungs, then back through exhalation valve and tube into the regulator, through reducing valve to cooler, and into breathing bag through exhalation tube and valve into lungs, and back through inhalation tube and valve into lungs, then back through exhalation valve and tube into the regulator, through reducing valve to cooler, and into breathing bag.
DETAILS OF THE McCAA TWO-HOUR OXYGEN BREATHING APPARATUS
ing men entering tanks and for general use inside of refining apparatus. Only one instance of poor protection was reported, attributed to improper construction of the mask; in all the other instances reported the men worked with perfect protection for periods of time up to an hour or more. One company has designed, for its own use, a hose mask that has the Tissot face piece and belt, and a flexible metal hose 1½ inches in diameter and 75 or 150 feet long. Air is drawn through the hose by the wearer himself. The hose is wound on a special reel and the apparatus is carried on a small autotruck when wanted in emergencies.

**SELF-CONTAINED OXYGEN BREATHING APPARATUS.**

The McCaa self-contained oxygen breathing apparatus of the half-hour type was developed by the Bureau of Mines at the request of the Navy Department especially for use in petroleum vapors. Plate VI, A, shows this apparatus; another type of the McCaa apparatus, designed to hold a two-hour supply of oxygen, is shown in Plate VI, B.

An oxygen breathing apparatus differs from a gas mask or a hose mask in that it carries, compressed into a tank at a pressure as high as 120 atmospheres (1,800 pounds per square inch), a supply of pure oxygen gas for the wearer. The oxygen is released through a series of valves, tubes, and rubberized bags, and inhaled through a mouthpiece. (In early types of oxygen breathing apparatus a "helmet" inclosed the head, but in late types the helmet is not used because it is dangerous.) The exhaled oxygen and carbon dioxide pass through a container of alkaline absorbent—caustic soda or soda-lime granules—which removes the carbon dioxide; the unused purified oxygen mixed with fresh oxygen from the tank is then rebreathed. The construction and performance of various self-contained oxygen breathing apparatus have been described elsewhere by the Bureau of Mines.²⁶

Details of the McCaa half-hour and two-hour apparatus are shown in Plates VII and VIII. Some important essential features are as follows:

1. **Automatic delivery of oxygen, controlled by the rate of consumption.** This provision eliminates waste and insures a full supply for breathing until the oxygen is actually consumed by the wearer.


79465°—24—3
(2) A hand-operated valve to deliver a continuous flow of oxygen through a by-pass around the automatic valve, in case the latter should not function.

(3) A refillable canister for holding the granular soda-lime absorbent for carbon dioxide. The soda lime, commercially known as "cardioxide," is easily added and removed.

(4) The weight of the half-hour apparatus is about 17 pounds and of the two-hour apparatus only 30 pounds. The latter is the lightest oxygen apparatus yet made for its respective time of usage.

(5) Breathing bags constructed of flexible stockinet fabric, rubberized on one side with a sheeting at least one-sixteenth inch thick. Tests have shown that the heavy rubberized fabric of the breathing bag excludes, for more than two hours, gasoline vapors in concentrations up to 30 per cent in air; thinly rubberized fabrics are quickly penetrated by gasoline vapors. Although the Bureau of Mines officially approved the Gibbs and the Paul oxygen breathing apparatus for use in irrespirable mine atmospheres after fires and explosions, it has not formally approved them for use in petroleum vapors because their thinly rubberized breathing bags may be penetrated.

At the present time the McCaa apparatus is not commercially available, but the Navy Department is requesting bids from manufacturers for constructing, according to McCaa designs and specifications, half-hour apparatus for use in the Navy. Thereafter the McCaa apparatus may be made for industrial uses. Only one type of apparatus now on the market—the Fleuss or Proto two-hour apparatus—has a breathing bag with walls thick enough to withstand penetration by petroleum vapors during a two-hour period.

The Bureau of Mines advises for the present that self-contained oxygen breathing apparatus, such as the Paul or the Gibbs, having thinly rubberized bags may be worn in petroleum vapors for periods not exceeding 10 minutes. Then the breathing bags should be removed and aired for a day in order to rid them of adsorbed vapor.

When the McCaa apparatus is manufactured commercially it will be generally available for protection against petroleum vapors. However, commercially produced apparatus will not be formally


28 Since this statement was written the Proto apparatus has been officially approved by the Bureau of Mines—in January, 1924.
approved by the Bureau of Mines until they have passed the tests and requirements of the Bureau's Schedule 13.29

One large oil company that has had considerable experience with various respiratory apparatus and has employees especially trained to wear self-contained oxygen breathing apparatus says that the apparatus with thinly rubberized bags has shown permeation in dense naphtha fumes; nevertheless, in ship bunkers where there are cross beams and pipes, the oxygen breathing apparatus is of advantage.

**COMPARISON OF GAS MASKS, HOSE MASKS, AND OXYGEN BREATHING APPARATUS.**

No one of the three types of oxygen breathing apparatus, gas mask, or hose mask can be selected as best for use in all conditions where respiratory protection is needed. Each condition must be considered as a problem in itself. The following summary will serve for comparing the types:

1. Gas masks are simplest, easiest to wear, and least cumbersome, but they protect only when the concentrations of noxious gases or vapors in air are relatively low.

2. Hose masks protect in any irrespirable atmosphere. They are somewhat cumbersome, however, and the length of hose limits the distance a wearer may go from fresh air.

3. Self-contained oxygen breathing apparatus protect in any irrespirable atmosphere. Their weight tends to tire a wearer, they can be used only by trained men, and they require frequent attention to insure maintenance in good working condition.

More complete statements on the properties of each apparatus in regard to various considerations are given in Table 4, which will aid selection of the type best suited for a given use.

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29 Procedure for establishing a list of permissible self-contained mine-rescue breathing apparatus, fees, character of tests, and conditions under which mine-rescue breathing apparatus will be tested: Schedule 13, Bureau of Mines, March 5, 1919, 12 pp.
### Table 4.—Comparison of advantages and limitations of gas masks, hose masks, and oxygen breathing apparatus for protection from petroleum vapors and from hydrogen sulphide.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Protection in atmospheres deficient in oxygen (less than 16 per cent oxygen).</td>
<td>Gas masks do not protect against atmospheres deficient in oxygen and should not be used therein. They serve only as filters for removing comparatively small amounts of irrespirable gas from air that is otherwise normal.</td>
<td>Hose masks protect against all deficiencies of oxygen, since they are not dependent on air surrounding wearer. Protect against any concentration.</td>
<td>Oxygen breathing apparatus protect against all deficiencies of oxygen. They are not dependent on surrounding air.</td>
</tr>
<tr>
<td>Protection in low concentrations of petroleum vapors (average 2 per cent and maximum 5 per cent in air).</td>
<td>Gas masks with canisters containing 600 c. c. or more of activated charcoal protect. Time of protection decreases rapidly as concentration increases. Canisters containing gas adsorbents other than activated charcoal are useless.</td>
<td></td>
<td>Do.</td>
</tr>
<tr>
<td>Protection in high concentrations of petroleum vapors (exceeding 5 per cent in air).</td>
<td>Gas masks do not protect well enough to assure safety. They should not be used.</td>
<td>Do.</td>
<td></td>
</tr>
<tr>
<td>Protection in low concentrations of hydrogen sulphide (average 1 per cent and not exceeding 2 per cent in air).</td>
<td>Gas masks with canisters containing 600 c. c. or more of soda lime or caustic soda fused on pumice granules protect. Time of protection decreases rapidly as concentration increases. Canisters of dry activated charcoal last only about one-fifth as long as those of soda lime.</td>
<td>Do.</td>
<td></td>
</tr>
<tr>
<td>Protection in high concentrations of hydrogen sulphide (exceeding 2 per cent in air).</td>
<td>Gas masks do not protect well enough to assure safety. They should not be used.</td>
<td>Do.</td>
<td>Do.</td>
</tr>
<tr>
<td>Protection against mixtures of hydrogen sulphide and petroleum vapors in air.</td>
<td>A canister containing a mixture of charcoal and soda lime should be used. Time of protection from gasoline depends on volume of charcoal in the mixture and against hydrogen sulphide chiefly on volume of soda lime. 600 c. c. soda lime plus 900 c. c. charcoal is a practical mixture.</td>
<td>Do.</td>
<td>Do.</td>
</tr>
</tbody>
</table>
Protection against Irrespirable atmospheres other than those above.

Charcoal canisters protect also against organic vapors, amylene, benzene, ether, toluene, and the like, in concentrations similar to those of gasoline; soda lime protects also against acid gases, chlorine, formic acid, hydrogen chloride, nitrogen peroxide, sulphur dioxide, and the like. They do not protect against carbon monoxide or ammonia. Full information concerning the gas in question and ability of gas masks to protect is necessary in each instance.

Knowledge of concentrations necessary to assure safety.

A knowledge of concentrations of gas and vapors in tanks and apparatus is necessary to assure that the wearer does not exceed the capacity of his gas mask to protect.

Instruction in use of apparatus needed by wearer to assure his safety.

Very little instruction is needed because gas mask is relatively simple. Care must be exercised to use the right type of canister.

Training needed to assure safety.

Very little training is needed. A few trials at adjusting mask and noting its tightness by closing canister inlet with the hand and inhaling to test for leakage suffice. No air should enter under these circumstances. Similar tests should always precede entrance to irrespirable gases and they should be entered cautiously while the wearer makes sure that his mask works properly.

Mechanical attention required to maintain good condition.

Very little attention is needed. Care should be exercised that no leakage exists, as negative pressure occurs during inhalation.

...do..........................  Do.

Not necessary.................  Not necessary.

Very little instruction is needed.

Statement under gas masks also applies to hose masks. If a blower is used to force air to wearer, effect of leaks is minimized because they are then outward.

Apparatus should be examined, tested, and overhauled as needed at intervals of about one month by a skilled mechanic or other competent person who understands thoroughly the action and function of each part. Failure to keep apparatus in perfect adjustment may jeopardize the wearer.
<table>
<thead>
<tr>
<th>Conditions</th>
<th>Gas masks</th>
<th>Hose masks</th>
<th>Oxygen breathing apparatus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of apparatus</td>
<td>About 4 to 8 pounds, according to size of canister and style of support.</td>
<td>Depends on length and type of hose. Wearer, however, supports only about 5 pounds.</td>
<td>30 to 45 pounds for various types of two-hour apparatus; 15 to 17 pounds for half-hour.</td>
</tr>
<tr>
<td>Encumbrance to wearer</td>
<td>Interferes relatively little with movements.</td>
<td>Hose is an impediment in some situations, especially when space is cramped or beams, pipes, or corners are numerous.</td>
<td>Encumbrance is considerable; weight, especially of heaviest types, become tiresome after a time.</td>
</tr>
<tr>
<td>First cost of apparatus</td>
<td>$15 to $50, according to manufacture and special features.</td>
<td>About $75.</td>
<td>About $160 to $225 for two-hour types; about $125 for half-hour types. Accessories such as oxygen tanks and pumps may add to expense.</td>
</tr>
<tr>
<td>Cost of adsorbents and oxygen</td>
<td>New canisters cost about $2 to $10, according to size and kind of adsorbent.</td>
<td>No costs.</td>
<td>Oxygen costs about 2 cents per cubic foot of gas at atmospheric pressure; soda lime costs about 35 cents per pound, or $1.40 per charge.</td>
</tr>
<tr>
<td>Cost of upkeep</td>
<td>Practically no cost until worn out or until rubber deteriorates with age.</td>
<td>Practically no cost until worn out or until rubber deteriorates.</td>
<td>Periodic attention and adjustment create some cost of upkeep. Rubber parts deteriorate with age and require replacement when leaks appear.</td>
</tr>
<tr>
<td>Safe period of continuous service</td>
<td>Safe period may range from a few minutes to several hours or even days, being about inversely proportional to the concentrations of the gases or vapors encountered.</td>
<td>There is no limit to safe period.</td>
<td>Oxygen breathing apparatus are made in two sizes rated for one-half and two hours' minimum supply of oxygen. When discharged they require renewal of oxygen and chemical charges.</td>
</tr>
</tbody>
</table>
SUMMARY AND CONCLUSIONS.

Gas masks, hose masks, and self-contained oxygen breathing apparatus were tested for respiratory protection against petroleum vapors (vapors of petroleums or petroleum products) and hydrogen sulphide. Conclusions are:

(1) The canister type of gas mask containing 600 c. c. of dry high-grade activated charcoal protects a wearer one hour or more against 1 per cent of gasoline vapor in air which is otherwise normal; that is, air having no deficiency of oxygen. It is not safe to use the canisters in uniform concentrations of gasoline vapor greater than 2 per cent nor in nonuniform or stratified concentrations averaging more than 2 per cent or anywhere exceeding 5 per cent. Moisture in charcoal reduces its capacity for petroleum vapors, therefore it should be kept dry. Used charcoal may be revivified by drawing air at 105° C. through a canister for two hours or more according to the size of the canister. Thus a canister may be used repeatedly.

(2) The 600-c. c. charcoal-filled canister mask protects against 1 per cent H₂S in air for 3½ minutes. Soda lime is a much better absorbent for H₂S; the 600-c. c. canister filled with soda lime lasting 17 minutes. Soda lime, however, does not protect against petroleum vapors and can not be regenerated. Mixtures of H₂S and petroleum vapors in air are adsorbed by charcoal, but each in proportion to its concentration reduces the adsorbent capacity of the charcoal for the other. Canisters containing both soda lime and charcoal adsorbents are of advantage when petroleum vapors and hydrogen sulphide are both encountered in considerable proportions. Gas masks should not be used in air exceeding 2 per cent of hydrogen sulphide or hydrogen sulphide plus petroleum vapor.

(3) Hose masks protect against any irrespirable atmosphere that the wearer’s skin will bear. Several types have been described. They are especially useful in tanks, apparatus, or situations where the distance from pure air is relatively short. A wearer can draw air by inhalation through 50 to 100 feet of three-fourths inch or larger hose without undue effort. However, a blower of the fan type that delivers air under either direction of rotation and does not when stopped retard the passage of air is of advantage. Compressed air, if available, may be used. Blowers reduce the effort imposed upon the wearer; also if leaks develop in the apparatus the leakage is outward. The need of an attendant to operate a blower promotes safety in an emergency. In fact, persons should not enter dangerous atmospheres unless attended by preferably two or more strong and competent persons to act in case of emergency, and the use of life lines attached to the body is advisable.
(4) Self-contained oxygen breathing apparatus having breathing bags coated with rubber at least one-sixteenth of an inch thick protect against any irrespirable atmosphere for periods as long as two hours, which is the nominal time for a charge of oxygen in the larger apparatus. Thinly rubberized breathing bags may be quickly penetrated by petroleum vapors. Both Gibbs and Paul apparatus, which have been officially approved by the Bureau of Mines for mine rescue and recovery work, are not advised for use in petroleum vapors for periods exceeding 10 minutes, because the vapors may penetrate the thin bags. After this period these bags should be aired for eight hours to free them of absorbed vapor.

(5) The McCaa oxygen apparatus was recently devised by the bureau especially for use in petroleum vapors. Its essential features are its light weight, a rubberized bag having walls thick enough to withstand petroleum vapors for at least two hours, and an automatic oxygen supply controlled by the rate of consumption. Two-hour and half-hour sizes were made. The McCaa apparatus is not on the market as yet, but manufacturers are expected to produce it soon.

PUBLICATIONS ON GAS MASKS AND BREATHING APPARATUS.

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PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION.


Miners' Circular 4. The use and care of mine rescue breathing-apparatus, by J. W. Paul. 1911. 24 pp., 5 figs.

Self-contained mine rescue oxygen breathing-apparatus, by D. J. Parker, G. S. McCaa, and E. H. Denny. 1923. 120 pp., 14 pls., 9 figs.

**PUBLICATIONS THAT MAY BE OBTAINED ONLY FROM THE SUPERINTENDENT OF DOCUMENTS.**

