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CALCIUM CARBIDE

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The present invention relates to improvements in the handling and storage of calcium carbide. It provides an improved calcium carbide container and also a method of packaging ordinary calcium carbide whereby the improved container may be obtained.

It is well known in the industry that calcium carbide which has been stored in a container or vessel has a marked tendency to generate actylene upon standing. This "after generation" of acetylene produces at least the following undesirable results: it wastes acetylene since the gas is being generated at times when it is not desired; and it creates an explosive hazard since the concentration of the resulting acetylene in air approaches or exceeds the minimum amount necessary for an explosive mixture, namely, 2.3% acetylene in air. The specific reactions occurring in a container to generate acetylene cannot be explained with certainty. Ordinary calcium carbide contains about 77% calcium carbide and 23% calcium oxide. Originally it was believed that the surface of the carbide becomes coated with calcium hydroxide or hydrated calcium oxide, which then reacts with the carbide to generate acetylene; that any water bound to the carbide also reacts with the carbide to generate acetylene; and that such reactions occur immediately.

From extensive tests, however, I have found that the reactions in the carbide container take place over a period of from four (4) to fourteen (14) days, and that the maximum acetylene concentration in a container will approach the range of 23 to 26% in a few days after the carbide has been packed. The acetylene concentration can be removed (1) by direct purging with a relatively inert gas such as nitrogen or (2) by a series of evacuating steps and subsequently filling the space above the bed of carbide wtih an inert gas. But either method of minimizing the acetylene concentration is commercially objectionable since both require the lapse of an aging period in the container before it may be purged to remove the excess acetylene. Moreover, it has been proposed to purge a vessel with nitrogen while it is in the process of being packed with carbide in an effort to raise the lower flammability limit of the acetylene-air mixture, and thus reduce the possibility of an explosive mixture. But even here, after generation of acetylene resulted in a concentration of from 18 to 26% acetylene; and in instances where the container or vessel breathed in air at ambient temperature or a leak developed, the acetylene concentration resulted in an explosive mixture. This situation occurs particularly in most industrial type containers since they are not considered airtight in the strictest sense.

The problem of handling calcium carbide safely became even more acute when it was discovered that calcium carbide in finely divided form may be utilized for treating molten ferrous metal to obtain an iron product having improved properties and characteristics. Unfortunately, the after generation of acetylene in a calcium carbide container increases in volume as the size of the carbide is decreased; in other words, the evolution of acetylene increases as the total surface area of calcium

carbide is increased. In United States Patent No. 2,577,764 assigned to the assignee of the present application, for example, there is disclosed and claimed a process for treating molten ferrous metal containing sulphur with finely divided calcium carbide to produce a reaction between the sulphur and carbide. A novel method of producing an improved gray cast iron by treating a molten cast iron composition with an agent comprising finely divided calcium carbide is disclosed and claimed in United States application Serial No. 305,315, also assigned to the assignee of the present application. The finely divided calcium carbide employed in these inventions may, for example, have a Tyler standard screen or sieve analysis of 100% minus 10-mesh and at least 50% plus 100-mesh.

From recent field experience, it was shown that a potentially hazardous explosive condition exists in a container packed with 20 mesh×0 calcium carbide to be used in the treatment of molten metal. The after generation of acetylene from such carbide in industrial containers amounts to 110 to 140 milliliters of acetylene per pound of calcium carbide. Such evolution has been measured and found to be in the range of 0.5% to 28.0% of the total air mixture in which the ordinary carbide is stored. It is obvious that in many instances acetylene concentrations in excess of 2.4% (lower flammability limit in air) exist in hoppers packed with finely divided or metallurgical calcium carbide, thus presenting a serious problem in the industry. The major generation of acetylene (about 85%) from the small sizes of carbide usually occurs in the first 36 hours after packing.

It appears desirable, therefore, to avoid as far as practical an excessive generation of acetylene from the calcium carbide in industrial containers which might lead to explosive violence.

One object of the present invention is to provide a novel method of storing calcium carbide safely, whereby an improved container for such material is obtained.

Another object of the invention is to eliminate any explosion hazard that may exist in calcium carbide containers.

A further object of the present invention is to provide an improved method of packaging calcium carbide whereby the after generation of acetylene in industrial carbide containers is arrested or greatly minimized, so that the concentration of acetylene in the atmosphere within the container is always less than the minimum amount necessary for an explosive mixture.

Still another object is to provide a method of packing finely divided calcium carbide in a commercially satisfactory manner whereby the necessity for purging the container after its initial packing is eliminated.

These and other desirable objects and advantages of the present invention will become more apparent from the following detailed description of the invention.

This invention is based mainly on the discovery that the addition of a small quantity of carbon dioxide to an industrial container in which finely divided calcium carbide is stored provides a container which is free of explosive mixtures even though it may not be completely airtight. While the present invention is applicable to all sizes of calcium carbide, it is particularly advantageous with respect to the smaller sized calcium carbide since the after generation of acetylene increases in volume as the size of the carbide is decreased. The carbon dioxide may be added in solid or gaseous form. From actual tests, it was found that the addition of carbon dioxide at the time the calcium carbide was placed in a shipping container resulted in a maximum concentration of 1% acetylene, which is less than one-half the usual lower explosive limit of acetylene in air mixtures (2.3%). Further, since the after generation of acetylene never exceeds about 1% after any particular period of time; the

necessity for purging the container after the aging period is entirely eliminated. By utilizing the present invention, therefore, the container may be sealed immediately after being freshly packed with calcium carbide.

The following examples will serve to illustrate the invention. For simplicity, the details as to amounts of calcium carbide stored in industrial containers and tested, volumes of carbon dioxide, and percentages of acetylene both after one day and after eighteen days are tabulated. In all the examples the size of calcium carbide was 20-mesh×0. One volume of carbon dioxide is defined as being equivalent to the volume occupied by the free air space in any particular vessel or container. Carbon dioxide was added to the container when the calcium carbide was being placed therein.

Table I

Sample No.	Calcium carbide, pounds	Carbon dioxide, volumes	Acetylene after 1 day, percent	Acetylene after 18 days, percent
B	500	3	0.2	0.8
C	500	3	0.2	0.6
D	500	4	0.0	1.0
E	500	4	0.0	1.0
F	500	5	0.2	0.8
G	500	5	0.2	0.9
H	300	6	0.2	1.0
I	5,000	3	0.25	0.85
J	10,000	3	0.2	0.6

In the above examples, the volume of carbon dioxide employed varied from three to six times the volume of the free air space within the vessel or container. These examples and additional tests indicated that optimum results are obtained when the volume of carbon dioxide is one-half (½) to six (6) times that of the free air space within the container, the preferred range of volume being between 2 and 4. It will be noted that the amount of acetylene generated after one day varied from 0.0 to 0.2%, and that the amount varied from 0.6 to 1.0% after 18 days, in sharp contrast to the 10 to 26% amount of acetylene generated after 4 to 18 days in containers as conventionally packaged in the industry. Further, since the concentration of acetylene in the novel container was well below 2.3%, no aging was required. In the tests, it was observed that the total inert gases, practically all nitrogen and carbon dioxide, ranged from 85 to 98% of the total gaseous mixture in the container. Varying ranges of oxygen content were recorded since normal atmosphere breathing occurs within the container. It was noted that the use of carbon dioxide did not detrimentally affect either the calcium carbide or the container therefor. The actual volume occupied by the calcium carbide in any one of the sample containers was slightly more than the volume occupied by the free air space therein.

The exact manner in which carbon dioxide acts to arrest the after generation of acetylene is not fully understood. It is thought that certain sites on the calcium carbide surface are the source of the acetylene which is slowly evolved from the carbide, and that the carbon dioxide is irreversibly adsorbed on such sites. The carbon dioxide may be reacting with either the strongly bound acetylene or some other chemical substance at these sites to form a protective layer which substantially minimizes or prevents evolution of acetylene. It is also possible that the carbon dioxide additon sufficiently stabilizes the calcium hydroxide or hydrated lime so that the water normally present in these compounds is unavailable for reacting with calcium carbide to produce acetylene. There is no doubt, however, that carbon dioxide raises the lower flammability limit of acetylene-air mixtures to about 4.0%.

When carbon dioxide was employed in gaseous form, it was delivered through a pipe extending to near the bottom of the vessel. A predetermined amount of calcium carbide was then placed in the container. After the desired amount of carbon dioxide gas had been introduced in the container, the feed pipe was removed, and the container was sealed in the conventional manner.

When carbon dioxide is used in the present invention in solid form, a small amount of calcium carbide is initially added to the vessel so as to cover the bottom; the solid carbon dioxide is then placed on top of the carbide; and calcium carbide is then added to complete the packing of the container, after which it is sealed. The amount of solid carbon dioxide added is that required to furnish the desired number of volumes measured in terms of free air space volume. In a 500 pound container, for example, optimum results are obtained when the weight of solid carbon dioxide used is from ¼ pound to 3 pounds, or from 0.05% to 0.60% of the carbide by weight, the preferred weight being from 1.0 to 2.0 pounds, or from 0.20% to 0.40% of the carbide. The lid or top of the container is provided preferably with a rubber diaphragm, check valve, or the like to release the pressure within the vessel as the carbon dioxide solid sublimes. From a commercial standpoint, the use of solid carbon dioxide is preferred since it can be added with a minimum amount of effort and cost.

It is evident that utilization of the present invention makes possible the handling and storage of calcium carbide in a commercially satisfactory manner. From the standpoint of safety, the novel container for calcium carbide is safer to handle and transport than are the conventional industrial containers, since the after generation of acetylene is arrested by the use of carbon dioxide. The maximum amount of acetylene generated in applicant's container is substantially less than the amount required to produce potential or actual explosions in air-acetylene mixtures. Calcium carbide packed in accordance with applicant's process does not deteriorate or prematurely generate a significant amount of acetylene, thus preserving the calcium carbide indefinitely until it is ready for use in the ordinary manner.

It is understood that the invention is not limited to the specific examples described herein, but may be practiced in other ways without departing from the spirit and scope of the invention as defined by the following claims.

What I claim is:

1. The method of conditioning a container for storing calcium carbide safely which comprises packing said container with finely divided calcium carbide, the carbide particles being of a fineness to pass through a 20-mesh screen, adding a small but effective amount of solid carbon dioxide whereby the maximum amount of acetylene generated from said carbide is always less than about 1.0% of the gaseous atmosphere within said container, said amount of solid carbon dioxide supplying a volume of carbon dioxide gas ranging from two to four times the volume of the free air space within said container, and sealing the container.

2. A unit for the safe handling and storage of calcium carbide comprising a sealed container, finely divided calcium carbide packed in said container, the carbide particles being of a fineness to pass through a 20-mesh screen, solid carbon dioxide in an amount sufficient to supply a volume of carbon dioxide gas ranging from two to four times the volume of the free air space within said container, a maximum amount of acetylene generated from said calcium carbide which is less than 1% of the gaseous mixture within said container, and said solid carbon dioxide ranging from about 0.05% to 0.60% of said calcium carbide by weight.

References Cited in the file of this patent

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