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DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
WASHINGTON

Letter
Circular
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SOLID CARBON DIOXIDE
(August 13, 1930.)

Solid carbon dioxide compressed into cakes is being manufactured for use as a refrigerant and sold under several trade names, such as "Dry Ice", "Carbonice", etc. These cakes of compressed solid carbon dioxide closely resemble packed snow in appearance and have a temperature of -109°F (-78.5°C) or lower. Carbon dioxide at room temperatures and atmospheric pressure is a colorless, odorless gas. It occurs in the atmosphere to the extent of about 0.03% by weight, is a product of combustion and respiration, and a by-product of fermentation and of many chemical processes. It can exist as a solid at atmospheric pressure only because of its very low temperature. The cakes are made by compressing in a mold carbon dioxide snow produced by expanding liquid carbon dioxide at a low temperature from a high pressure to atmospheric pressure. In the expansion, part of the liquid is changed to a solid in the form of snow; the rest becomes a gas which is returned to the compressor for recompression and the making of more snow.

Carbon dioxide is different from water and most other substances in that it cannot exist as a liquid at atmospheric pressure (14.7 lbs. per sq. in.)* Only when the pressure is equal to or greater than 75.1 pounds per square inch (5.1 normal atmospheres) and its temperature -70°F (-56.6°C) or higher (the "triple point" pressure and temperature) can carbon dioxide exist as a liquid. Hence instead of melting to a liquid as ice does, solid carbon dioxide <u>sublimes</u>, that is, it passes directly from the solid to the gaseous state. This is one of the great advantages of solid carbon dioxide when used as a refrigerant. It does not wet spaces, packages, and materials refrigerated with it, and all the inconveniences due to the water from melting ice are avoided.

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* An excellent discussion of this subject has been written by C.H.Meyers for "Ice and Refrigeration". See "Carbon Dioxide in the Solid, Liquid and Vapor States", Vol. 76, pp. 535-37, 1929.

Density: The density of the commercial product depends upon the pressures applied in compressing the loose solid into cakes, and possibly on the manner of compressing it. A sample tested at the Bureau of Standards weighed 79 pounds per cubic foot, or 1.27 grams per cc, which may be compared with 57 pounds per cubic foot or 0.92 gram per cc for ordinary ice. Crystalline carbon dioxide made by freezing liquid carbon dioxide weighs about 96 pounds per cubic foot, or 1.53 grams per cc, (International Critical Tables, Vol. I, p. 112 and Vol. III, p. 43).

Temperature: The temperature of solid carbon dioxide surrounded by pure, gaseous carbon dioxide at a pressure of one normal atmosphere is -109°F or -78.5°C (International Critical Tables, Vol. III, p. 207). In contact with air, its temperature is lower because the partial pressure of carbon dioxide gas is less. In contact with quiescent dry air a temperature of -114°F has been observed and in air currents even lower temperatures are observed.

Vapor Pressure: Pure solid carbon dioxide inclosed in a container in contact with its own vapor exerts a pressure, known as the vapor pressure, which varies with the temperature of the solid. The following table, which is an unpublished correlation made at the Bureau of Standards of various data, shows the variation of the vapor pressure of carbon dioxide with temperature.

Temperature °F	Absolute Pressure lbs./sq.in.	Absolute Pressure Normal Atmospheres	Temperature °C
-69.8	75.1	5.11	-56.6
-75	61.7	4.20	-59.4
-80	50.8	3.46	-62.2
-85	41.6	2.83	-65.0
-90	33.9	2.31	-67.8
-95	27.5	1.87	-70.6
-100	22.2	1.51	-73.3
-105	17.8	1.21	-76.1
-110	14.2	0.97	-78.9
-120	8.9	0.61	-84.4
-130	5.4	0.37	-90.0
-140	3.2	0.22	-95.6

The normal atmosphere is defined as a pressure exerted by a column of mercury 76 cm high under standard conditions and is very closely equal to a pressure of 14.7 pounds per square inch.

Latent Heat of Sublimation: In passing from the solid to the gaseous state at atmospheric pressure carbon dioxide takes up 248 Btu of heat energy per pound, or 138 calories per gram, (International Critical Tables, Vol. V, p. 138). A Btu (British Thermal Unit) is by definition the quantity of heat energy required to raise the temperature of one pound of water 1°F.

Latent Heat of Fusion: In passing from the solid to the liquid state at its "triple point" (-70°F or -56.6°C) carbon dioxide takes up 82 Btu of heat energy per pound, or 45.3 calories per gram (International Critical Tables, Vol. V, p. 131).

Specific Heats of Solid and Gaseous Carbon Dioxide at Low Temperatures: The specific heat of solid carbon dioxide at -109°F (-78.5°C) is 0.31 Btu per pound per °F or calorie per gram per °C; that is, in order to raise or lower the temperature of one pound of solid carbon dioxide 1°F at -109°F, 0.31 Btu of heat energy has to be added to or taken from the solid, accordingly as its temperature is to be raised or lowered (International Critical Tables, Vol. V, p. 95). In the temperature interval between -109°F (-78.5°C) and +32°F (0°C) the mean specific heat of the vapor is about 0.19 Btu per pound per °F or calorie per gram per °C. Therefore one pound of carbon dioxide vapor after subliming from the solid will absorb 0.19 Btu for each degree rise in temperature between -109°F and +32°F (International Critical Tables, Vol. V, p. 80).

Refrigerating Effect: Besides the refrigerating effect due to the change of state, there is the additional refrigerating effect of 27 Btu per pound at 32°F (15 calories per gram at 0°C) equal to the amount of heat which the cold carbon dioxide vapor at -109°F (-78.5°C), after subliming from the solid, absorbs in being warmed to 32°F (0°C). Hence one pound of carbon dioxide absorbs 275 Btu, or 153 calories per gram, in changing from a solid at -109°F (-78.5°C) to a gas at 32°F (0°C). This is approximately equal to twice the amount of heat, 144 Btu per pound or 79.6 calories per gram absorbed by ice on melting at 32°F (0°C); and, as this is often

expressed, one pound of solid carbon dioxide has approximately the same refrigerating effect at 32°F as two pounds of ice.

Mixtures of ice and salt are used to produce temperatures below 32°F and to refrigerate spaces at temperatures below those obtainable with ice alone. The heat absorbed by a pound of a mixture of ice and salt when the ice melts and the salt dissolves - its refrigerating effect - is smaller than the heat absorbed by one pound of ice, inasmuch as a pound of the mixture contains less than a pound of ice, the salt affecting the result only to a comparatively small extent. Moreover, the latent heat of fusion of ice is smaller at lower temperatures than it is at 32°F, and some of the ice is melted in cooling the mixture of ice and salt to the reduced temperature. These effects lower somewhat the amount of refrigeration which can be obtained from ice when it is used with salt. Hence, the ratio of the refrigerating effect of solid carbon dioxide to that of ice used with salt is greater than the ratio of their refrigerating effects when ice is used alone.

As solid carbon dioxide is ordinarily used as a refrigerant, the cold carbon dioxide gas as it sublimes from the solid displaces from the space to be refrigerated first the air and then the warm carbon dioxide gas. Gaseous carbon dioxide is a better heat insulator than air, the ratio of the heat conducted by carbon dioxide to that conducted by air under the same conditions at 32°F being 0.6. The heat, however, that passes from a warm exterior into a refrigerated space depends, among other things, upon the insulating properties and upon the thickness of the separating walls as well as upon the thermal conductivity of the gas inside. The better the heat insulation of the separating walls, the relatively less important is the thermal conductivity of the gas inside.

Uses: Solid carbon dioxide has been used most extensively for refrigerating ice cream in transit. It is also used for refrigerating shipments of other perishable commodities.* In laboratories it is used to some extent for the production and maintenance of low temperatures for testing and experimental work.

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* Carbon dioxide atmospheres have been found to produce harmful effects on living things kept in them. For this reason carbon dioxide atmospheres exercise a preservative

action on meats and fish by impeding the growth of bacteria in them (See reference (10) of the "Bibliography" at the end of this letter circular). Since fruits, even after they are picked from the plant, are living things which take up oxygen and give off carbon dioxide, high concentrations of carbon dioxide in an atmosphere, in which they are stored, for short times or smaller concentrations for longer times are harmful. For further information on this subject, the reader is referred to the Bureau of Plant Industry, Department of Agriculture, Washington, D. C.

Machinery for Making Solid Carbon Dioxide: The names and addresses of some companies which manufacture machinery used in the production of solid carbon dioxide are given below in alphabetical order.

(1) Brunswick Kroeschell Company, New Brunswick, New Jersey.
(2) Dry Ice Equipment Corporation, 52 Vanderbilt Avenue, New York.
(3) Frick Company, Waynesboro, Pa.
(4) Wittenmeier Machinery Company, Chicago, Ill.
(5) York Manufacturing Company, York, Pa.

Bibliography: The following is a list of references to papers on the manufacture and use of solid carbon dioxide as a refrigerant, arranged in the order of publication:

(1) Several Articles on Dry Ice in "The Canadian Fisherman", Gardenvale P. Q. Canada; Vol. 11, No. 5 (May, 1924).
(2) "Solid CO_2 in the Fish Industry", by H. F. Taylor in Ice and Refrigeration; Vol. 71, pp. 211-13 (1926).
(3) "Ice that Melts to a Gas", by D. H. Killeffer, Scientific American; Vol. 137, pp. 220-222 (1927).
(4) "Solid CO_2 a New Commercial Refrigerant", by D. H. Killefer, Journal of Industrial and Engineering Chemistry; Vol. 19, pp. 192-5 (1927).
(5) "The Field of Dry Ice in Modern Refrigeration", by I. W. Martin, Jr., Refrigerating Engineering; Vol. 15, pp. 33-34 (1928).
(6) "The Commercial Field for Dry Ice", Refrigerating Engineering; Vol. 16, No. 2, pp. 45-46 (August, 1928).
(7) "Manufacture of Carbon Dioxide", by H. E. Howe, Journal of Industrial and Engineering Chemistry, Vol. 20, pp. 2091-4 (1928).

(8) "Carbon Dioxide in the Solid, Liquid, and Vapor States", by C. H. Meyers, Ice and Refrigeration; Vol. 76, pp. 535-7, June, 1929.
(9) "Dry Ice Manufacture", by J. C. Goosman, Refrigerating Engineering; Vol. 18, p. 155 (December, 1929).
(10) "Carbon Dioxide Preservation of Meat and Fish", by D. H. Killeffer, Journal of Industrial and Engineering Chemistry; Vol. 22, pp. 140-3 (1930).
(11) "Hydrated Solid Carbon Dioxide", by W. S. Josephson, Refrigerating Engineering; Vol. 19, p. 25 (1930).
(12) "The Design and Specifications of a Dry Air Refrigerator Car", by C. C. Palmer, Refrigerating Engineering; Vol. 19, No. 2, p. 67 (1930).
(13) "Solid CO_2 as a Refrigerant", by F. W. Rabe, Refrigerating Engineering; Vol. 19, No. 5, pp. 143-145 (1930).
(14) "Truck Body Refrigeration", by William F. Baird, Refrigerating Engineering, Vol. 20, p. 16 (1930).