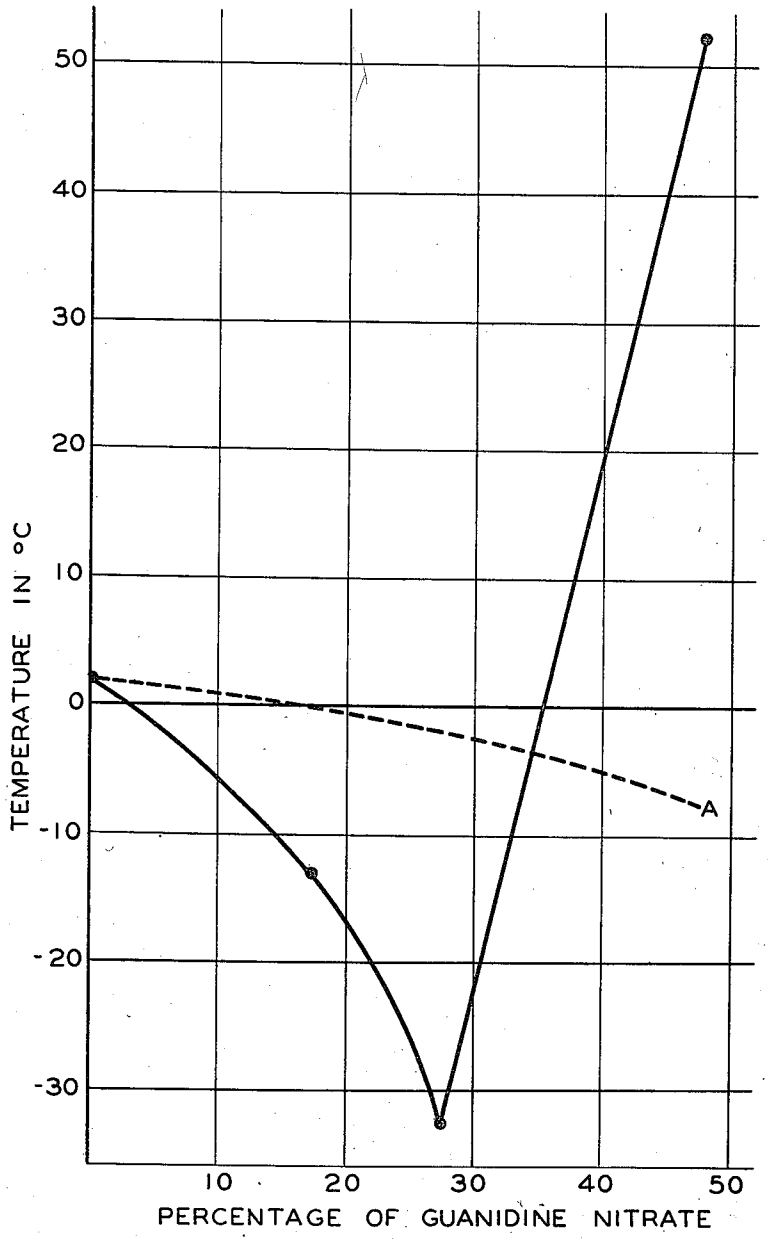
Oct. 30, 1956 D. W. RYKER 2,768,888

HYDRAZINE

Filed June 24, 1953



INVENTOR.
DON W. RYKER
BY
Clelle W. Upchurch
AGENT

United States Patent Office 2,768,888 Patented Oct. 30, 1956

2,768,888

HYDRAZINE

Don W. Ryker, Alton, Ill., assignor to Olin Mathieson Chemical Corporation, a corporation of Virginia

Application June 24, 1953, Serial No. 363,814

2 Claims. (Cl. 52—.5)

This invention relates generally to hydrazine and to water solutions thereof and more particularly to hydrazine compositions having advantageous freezing points and to a method for making them.

It has been proposed heretofore to use hydrazine or compositions of hydrazine hydrate or hydrazine and water as a fuel in internal combustion engines, jet-propelled heavier-than-air craft, and as a propellant in rockets and ammunition cartridges. Hydrazine has proven to be one of the most efficient compounds available for these purposes and has three of the four primary requisites of an ideal fuel, namely, (1) high density, (2) low viscosity, and (3) low molecular weight combustion products. Hydrazine is not entirely suitable for the purpose, however, because its freezing point is about 2° C. and will thus solidify at high altitudes or under some weather conditions and become ineffective as a fuel.

It is therefore an object of this invention to provide a hydrazine composition adapted for use in rockets, jet propelled devices, internal combustion engines, ammunition cartridges and similar devices which is devoid of the foregoing disadvantages of prior art hydrazine compositions. It is another object of this invention to provide a hydrazine composition having a freezing point below that of anhydrous hydrazine. A further object of the invention is to provide a hydrazine composition especially well suited for use as a fuel at high altitudes and in the colder regions of the world. A still further object of the invention is to provide a method for making hydrazine compositions having an advantageous freezing point.

Other objects and advantages will be apparent from the following description and accompanying drawing which illustrates the freezing point curve of hydrazine-guanidine nitrate mixtures with the weight percent of guanidine nitrate as abscissa and the freezing point temperatures in °C. as the ordinate.

It has been found in accordance with this invention that the foregoing objects as well as others can be achieved by providing hydrazine compositions containing guanidine nitrate. The hydrazine composition may be formed from aqueous or anhydrous hydrazine. By "hydrazine" as used in the appended claims is meant, therefore, aqueous solutions of hydrazine as well as anhydrous hydrazine. Guanidine nitrate is a solid and crystals thereof can be added to the hydrazine composition. Whereas guanidine nitrate has been found advantageous for the purpose, some homologous compounds including nitroguanidine and triaminoguanidine nitrate have been found unsuitable for the purpose.

It is, of course, well known that the freezing or melting point of a compound is in general lowered by the inclusion therein of an impurity or other compound. In fact, the amount of lowering of the freezing point to be expected by a given amount of another compound may be calculated in accordance with the equation

$$\text{Log}_e(1-n)=\frac{-L_f}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right)$$

which is derived from the Clapeyron equation and Raoult's law where n=mole fraction of solute, L_f=heat of fusion of the solvent, R=gas constant, T=freezing point of the solution or mixture, and T_m=melting point of the solvent. Referring to the drawing the broken line A, indicates the freezing point to be expected by the addition to hydrazine of guanidine nitrate. The points for the curve A, were calculated from the foregoing equation.

It has been discovered, however, that mixtures of hydrazine and guanidine nitrate do not follow Raoult's law and that the freezing point of a mixture thereof can not be predicted from the foregoing equation. On the contrary, as it will be noted from the solid line curve of the drawing which represents the freezing point curve of hydrazine and guanidine nitrate mixtures the freezing points are unexpectedly lower than would be predicted. For example, it is possible to lower the freezing point of hydrazine from about 2° C. to about —32° C. by adding about 27.5 percent by weight guanidine nitrate. As shown by the curve of the drawing, additions of larger percentages of guanidine nitrate indicate that this concentration is the eutectic point. Actually, as indicated, larger quantities of up to about 35 percent guanidine nitrate, can be added and a depression of the freezing point obtained, but obviously utilization of amounts up to that required to reach the eutectic point are preferred, although compositions are contemplated which contain any amount of the freezing depressant and have a freezing point below that of hydrazine.

Although some water does not deleteriously effect the ignitability of the hydrazine composition amounts of water greater than about one part water per part of hydrazine are not particularly desirable in fuels or propellants. Substantially anhydrous hydrazine, say about 95 percent to 100 percent hydrazine is preferred for such combustion purposes.

Because of the solubility or miscibility of guanidine nitrate, no difficulty is encountered in formulating improved hydrazine compositions in accordance with this invention. They may be readily prepared by merely mixing the constituents together in such proportions or amounts as set forth hereinbefore depending upon the freezing point desired. The only precautions necessary are those incident to handling hydrazine, which precautions are known to the art. It has been found that the compositions provided by the invention are stable under a variety of conditions so mixing just prior to use is not a requisite.

As an example, as illustrated in the accompanying drawing, a low freezing point composition suitable for a fuel may be prepared in accordance with one embodiment of this invention by mixing about 27.5 parts guanidine nitrate with about 72.5 parts of hydrazine whose composition is about 95 percent hydrazine and about 5 percent water. The crystals of guanidine nitrate can be conveniently poured into the hydrazine from any suitable container therefor such as the one in which it is weighed. The mixing may be accomplished at room temperature and, when the guanidine nitrate has dissolved a hydrazine composition is obtained having a freezing point of about —33° C. Compositions having freezing points anywhere within the range of —33° C. to the freezing point of hydrazine may be obtained in accordance with a process similar to that just described except the quantity of freezing point depressant is varied as indicated by the curve shown in the drawing.

The freezing point depressant of this invention, in general, continues to exhibit the faculty of depressing the freezing point of hydrazine compositions even when compatible compounds other than hydrazine and water are included therein. Hydrazine compositions having hy-

drazine as the major constituent thereof and having the freezing point depressant incorporated therein and also containing the usual additives to fuels such as, for example, coloring agents, accelerators, stabilizers, retardants, or other modifiers or hydrazine compositions incorporated in other fuels are therefore contemplated by this invention.

While specific compositions have been described in detail in the foregoing, various changes will occur to and can be made therein by those skilled in the art without departing from the spirit and scope of this invention and the invention is not limited to such details except as set forth in the appended claims.

Having thus described the invention, what is claimed and desired to secure by Letters Patent is:

1. As a new composition of matter, a substantially anhydrous mixture of hydrazine and guanidine nitrate

in the ratio of about 72.5 parts hydrazine and about 27.5 parts guanidine nitrate.

2. A method for lowering the freezing point of substantially anhydrous hydrazine which comprises dissolving therein about one part guanidine nitrate in about three parts hydrazine.

References Cited in the file of this patent

UNITED STATES PATENTS

2,159,234	Taylor	May 23, 1939
2,521,026	Solomon	Sept. 5, 1950
2,555,333	Grand et al.	June 5, 1951

OTHER REFERENCES

Klein: SAE Journal, December 1947, p. 25.