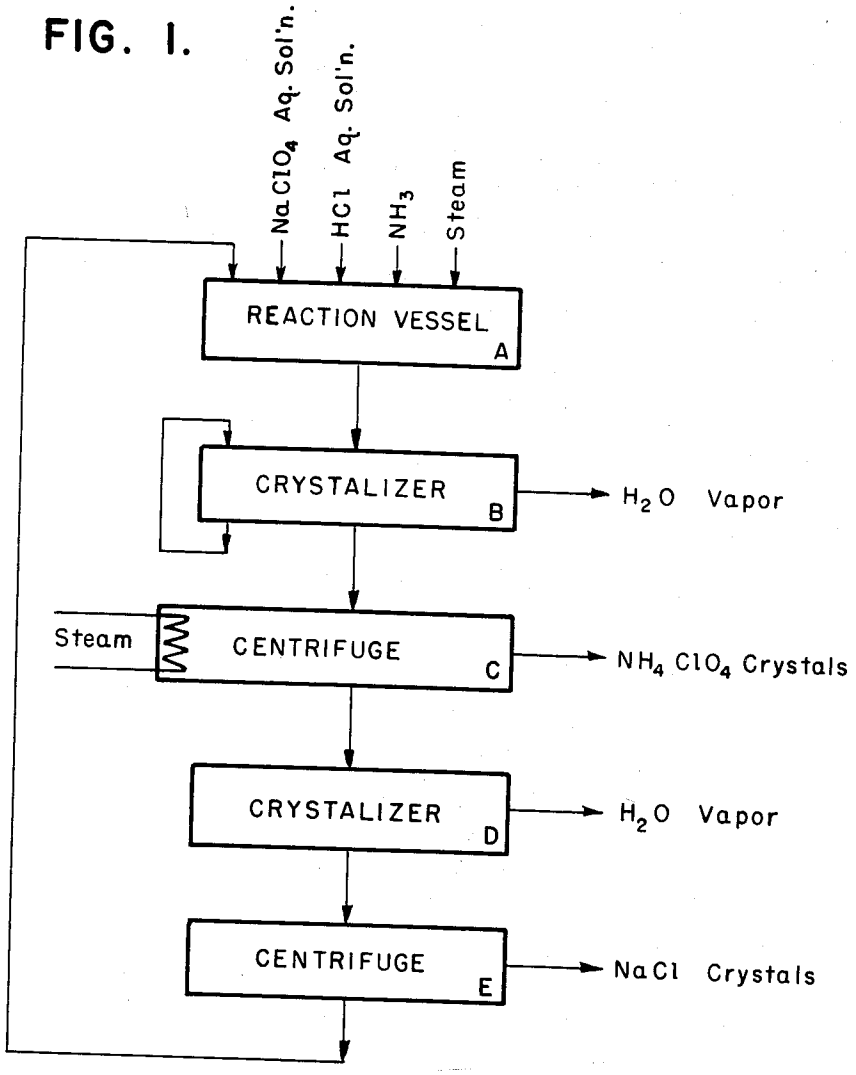
March 27, 1956 J. C. SCHUMACHER 2,739,873

PROCESS FOR MAKING AMMONIUM PERCHLORATE

Filed Sept. 25, 1952

2 Sheets-Sheet 1

FIG. 1.



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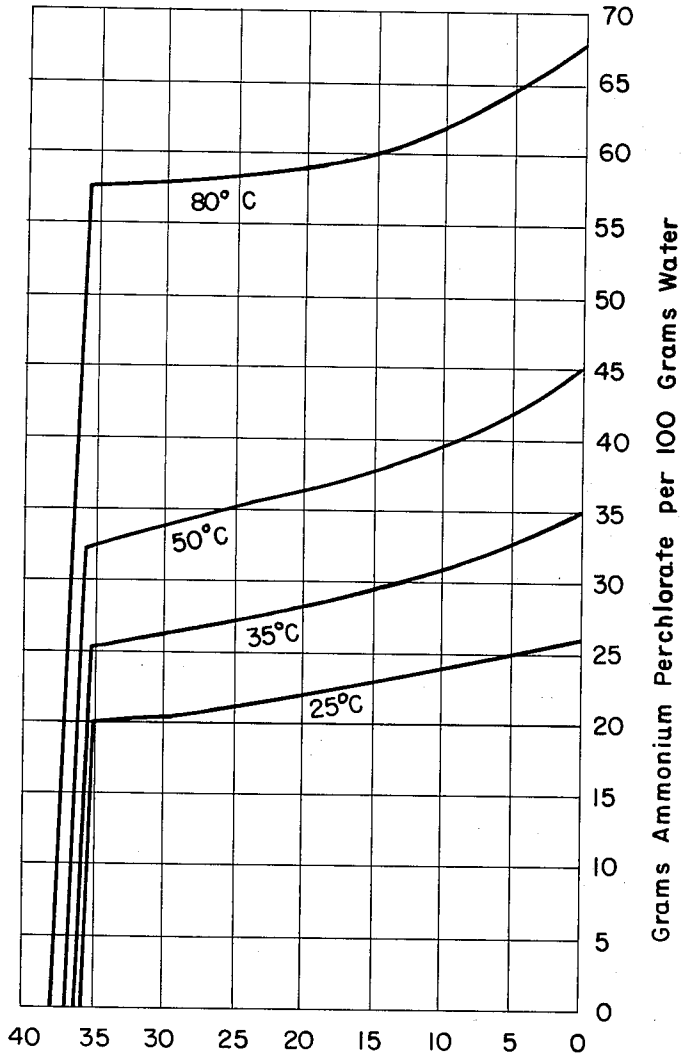
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FIG. 2.



MUTUAL SOLUBILITY CURVES FOR AMMONIUM PERCHLORATE – SODIUM CHLORIDE SYSTEM

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PROCESS FOR MAKING AMMONIUM PERCHLORATE

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3 Claims. (Cl. 23—85)

This invention relates to a process for making ammonium perchlorate.

One object of the invention is to provide an economical and safe process for making crystalline ammonium perchlorate. Another object is to provide a process for the continuous production of crystalline ammonium perchlorate. A further object is to provide a process for making ammonium perchlorate which is free from contamination by materials deleteriously effecting its stability against explosion.

A still further object is to provide properly sized particles of ammonium perchlorate for subsequent use in propellants.

These and other objects are attained by my invention which will be understood from the following description, reference being made to the accompanying drawings in which

Fig. 1 is a diagrammatic representation of the process in its preferred form;

Fig. 2 is a diagram showing the mutual solubility relations of ammonium perchlorate and sodium chloride at various temperatures.

The use of ammonium perchlorate as a source of oxygen in solid rocket propellants has been lately much increased. Ammonium perchlorate is a white crystalline salt containing more than 50 percent by weight of oxygen and will detonate under powerful impulse and is therefore both an oxidizing agent and an explosive. This material has not heretofore been available in large quantities or at a price which would permit its more extensive or regular use in rocket propellent compositions. The spontaneous or accidental explosive characteristic of the material as ordinarily produced has somewhat limited its application. It has now been found that by eliminating all traces of chlorates and of organic matter, a relatively stable ammonium perchlorate may be produced. A product may be produced of the most desirable range of crystal sizes for storage, and for subsequent grinding to the desired sizes for use in rocket propellants. Ammonium perchlorate for propellants is usually prepared by suitable grinding to get a desired range of particle sizes immediately before fabrication into charges, since it has been found that finely pulverized ammonium perchlorate if allowed to stand after grinding, tends to form aggregates. The crystals produced by my process are of the best range of small sizes for storage, and also of the best range of sizes to require a minimum of grinding just prior to fabrication in propellant charges.

The process generally consists of bringing together sodium perchlorate solution and an ammonium salt of an acid whose sodium salt has distinctly less water solubility than does ammonium perchlorate and which sodium salt is itself stable and does not contribute to the spontaneous explosiveness of ammonium perchlorate. The aqueous solution thus produced is then concentrated until crystals of ammonium perchlorate separate, following which the ammonium perchlorate crystals are separated from the solution, washed and dried. The mother liquor is then

further concentrated until the sodium salt of the selected acid crystallizes following which these sodium salt crystals are removed and the mother liquor containing both ammonium perchlorate and the sodium salt is returned to the original reaction vessel for again serving as the liquid medium for carrying out the process.

The process will be illustrated in its preferred form which involves the use of liquid anhydrous ammonia, aqueous hydrochloric acid and a solution of sodium perchlorate. Referring now particularly to Fig. 1, suitable proportions of the ingredients liquified ammonia, aqueous hydrochloric acid and an aqueous solution of sodium perchlorate are introduced into the reaction vessel A, along with the mother liquor returned from the process as will be described. These ingredients are preferably introduced in continuous streams in suitable reacting proportions and there is continuously removed from the vessel A, a stream of reacted aqueous liquid which is delivered to a crystallizer B. The crystallizer B consists of a closed vessel having a means for continuously circulating the incoming stream from the vessel A with the material already present in the vessel while water vapor is continuously removed by reducing the pressure in the crystallizer. The ammonium perchlorate crystals which are suspended in the liquid medium are permitted to grow until they have reached a selected small size which is considered to be most desirable for the particular propellant purpose. A continuous stream of slurry containing the carrier solution and the grown crystals of ammonium perchlorate is withdrawn from the crystallizer B and the crystals separated from the liquid in a continuous centrifuge C. The crystals of ammonium perchlorate are then further purified by surface washing, following which the adhering surface water is removed in a suitable drier. The carrier solution from the centrifuge is then delivered in a continuous stream to the salt crystallizer D. This crystallizer is similar to crystallizer B in that it is a closed vessel subjected to reduced pressure by means of which water vapor is continuously removed to concentrate the carrier solution, additional heat being supplied as required for the evaporation, by steam coils or the equivalent. The sodium chloride crystals which are produced are delivered continuously from the crystallizer D and separated from the mother liquor in the continuous centrifuge E, the crystals being washed, dried and recovered, or discharged as waste. The mother liquor from the centrifuge E is then returned in a continuous stream to the reaction vessel A and is recycled in the process.

The hydrochloric acid used is preferably that known as 22° Baumé and the ammonia is liquefied and substantially anhydrous. The sodium perchlorate solution which is delivered to the reaction vessel A is preferably about 66 percent by weight sodium perchlorate dissolved in water, this material being free from chlorates. A temperature of about 90° C. is maintained in the reaction vessel A and the heat for maintaining this temperature is derived from the hot mother liquor returning from centrifuge E and by the heat developed by the exothermic reaction of the liquid ammonia with the hydrochloric acid. Additional heat may be supplied in the form of live steam introduced into the reaction vessel.

As a specific example of the solutions which have been used in this process, given for purposes of illustration and not as limiting concentrations, I have supplied to the vessel A, anhydrous ammonia at the rate of 640 pounds per hour, hydrochloric acid of 22° Baumé at the rate of 3918 pounds per hour, and aqueous sodium perchlorate solution, 56 per cent by weight, at the rate of 8290 pounds per hour. There was also delivered to the reaction vessel A at the rate of 10,880 pounds per hour the mother liquor from the end of the process containing about 30

percent of ammonium perchlorate and 15 percent of sodium chloride, by weight. A continuous stream of reacted liquid was removed from the reaction vessel A to the crystallizer B, at the rate of about 45 gallons per minute, containing about 30 percent ammonium perchlorate and 15 percent of sodium chloride by weight. In crystallizer B there was removed water vapor at the rate of about 1880 pounds per hour, which reduces the temperature to about 35° C., and there was removed continuously from said crystallizer B a mixture of liquor and crystals of ammonium perchlorate in substantially the same quantity as received into said crystallizer less the water vapor removed. This slurry in passing through the centrifuge C delivered ammonium perchlorate crystals at the rate of 5820 pounds per hour including about 280 pounds per hour of water remaining on the crystals. The centrifuge C also delivered a carrier liquid composed of 20 percent sodium chloride, 15 percent ammonium perchlorate and about 65 percent water, by weight, at the rate of 19,740 pounds per hour, this carrier liquor going into the salt crystallizer D at the same rate. In the salt crystallizer, operated at about 80° C., approximately 7000 pounds per hour of water was removed, forming about one ton of sodium chloride crystals per hour. The mixture of salt and solution from the crystallizer D is delivered at the same rate less the water vapor to the salt centrifuge E which separates approximately one ton per hour of sodium chloride crystals, and about 10,880 pounds per hour of mother liquor as previously described which is returned to the reaction vessel A.

The process may be operated continuously as described or it may be operated batch-wise following substantially the same process steps as indicated, using storage tanks between steps where required.

The process may be modified by introducing into the reaction vessel A a water solution of ammonium chloride in an equivalent amount to that previously indicated (sufficient to react with the sodium perchlorate) in which case it is necessary to add more heat to bring the reaction vessel to the desired operating temperature of about 90° C.

Other mineral acids than hydrochloric acid may be used, for example, carbonic acid (from carbon dioxide gas), phosphoric acid, sulphuric acid, or their equivalent acids.

The mutual solubility relations of sodium chloride and ammonium perchlorate are shown in the diagram of Fig. 2 for certain selected temperatures. Because of the low temperature gradient of solubility of sodium chloride and the relatively high temperature gradient of solubility of ammonium perchlorate, it is possible to fractionally separate the prepared ingredients as described. If other salts than those of hydrochloric acid are employed, a suitable fractional crystallization process would be used, depending upon mutual solubility relations of the involved salts.

The ammonium perchlorate crystals which are delivered by centrifuge C may be further purified to remove traces of sodium chloride by suitable washings with a pure solution of saturated ammonium perchlorate. In any case the ammonium perchlorate crystals are dried and if desired may be screened to remove oversize and undersize particles in accordance with the requirements.

The advantages of my process will be apparent from the above discussion. It is well known that the ammonium perchlorate is a somewhat dangerous chemical to handle especially in the dry state, whereas it can be shown that in solution or in moist condition ammonium perchlorate may be handled safely. The process of my invention is carried out in water solution or at least in a wet state except for the final stage of drying and screening the ammonium perchlorate crystals. The process has

the advantage that only small amounts of steam or power are required. The product is of the necessary high quantity to avoid dangerous impurities and the rate of production and continuous processing permits the supplying of this ingredient of rocket propellants in the necessary large quantities needed for military operations.

I claim:

1. A continuous process for making ammonium perchlorate comprising continuously feeding in and reacting liquid ammonia, aqueous hydrochloric acid and aqueous sodium perchlorate solution in a reaction mass consisting of a mother liquor containing essentially sodium chloride and ammonium perchlorate in aqueous solution, said reaction being at temperatures of about 90° C.; continuously removing a stream of said mother liquor with the contained reaction products from the reaction zone; cooling said stream and continuously removing water vapor and crystals of ammonium perchlorate from said stream of mother liquor; heating said stream of mother liquor from which ammonium perchlorate crystals have been removed and continuously removing water vapor and crystals of sodium chloride from said stream; and continuously returning said mother liquor containing sodium chloride and ammonium perchlorate in aqueous solution to said reaction mass in said first step.

2. A continuous process for making uniformly sized ammonium perchlorate crystals comprising continuously reacting liquid ammonia, aqueous hydrochloric acid and aqueous sodium perchlorate solution in a circulating reaction mass of mother liquor containing essentially sodium chloride and ammonium perchlorate in aqueous solution, said reaction being at temperatures of about 90° C.; continuously removing a stream of said mother liquor with the contained reaction products from said mass; cooling said removed stream at a rate to produce ammonium perchlorate crystals of selected uniform size for use in jet propellants; and continuously separating out said crystals of ammonium perchlorate from said stream of mother liquor.

3. A continuous process for making uniformly sized ammonium perchlorate crystals comprising continuously reacting liquid ammonia, mineral acid and aqueous sodium perchlorate solution in a circulating reaction mass of mother liquor containing essentially the sodium salt of the mineral acid and ammonium perchlorate in aqueous solution, said reaction being at temperatures of about 90° C.; continuously removing a stream of said mother liquor with the contained reaction products from said mass; cooling said removed stream at a rate to produce ammonium perchlorate crystals of selected uniform size for use in jet propellants; and continuously separating out said crystals of ammonium perchlorate from said stream of mother liquor.

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