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# HEAT-PRODUCING COMPOSITIONS

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This invention relates to new and improved compositions for the production of heat and to methods of preparing the same. The invention is particularly concerned with compositions consisting of a mixture of dry ingredients which are capable of reacting rapidly to liberate heat when admixed with water.

Mixtures of chemical agents for this purpose have long been in common use for supplying heat to so-called fireless cookers, for the cleaning of grease clogged drains, and for other purposes in which the generation of heat is required. A mixture frequently employed for this purpose includes as its essential heat-producing ingredients aluminum and an alkaline agent such as sodium or potassium hydroxide, the addition of water to the mixture causing the aluminum and alkali to react rapidly, producing both heat and mechanical agitation.

Heat-producing mixtures of this type may, and preferably do, include, in addition to the principal heat-producing ingredients, such additional ingredients as may further the desired action, either to increase the production of heat or for other purposes incidental to the use for which the mixture is designed. For instance, oxidizing agents, such as sodium nitrate, are commonly employed to react with the hydrogen released during the principal reaction. Catalytic agents, additional heat-generating agents, such as sodium chlorite, and inert ingredients acting merely as carriers or fillers, such as sodium chloride, may be employed. In general, whatever the constitution of the whole mixture, it is common practice to limit the aluminum content to a range of about 2 percent to about 8 percent by weight of the total composition, the alkaline agent being employed in an amount at least about twice that required for combination with the aluminum, often constituting the major ingredient of the composition.

The uniformity of distribution of the various ingredients of the mixture is an important factor in determining the efficiency of the composition and poses a difficult problem in large scale production where it is essential that each small sample, of the amount which might be used in practice, truly and accurately represents the composition of the whole batch. Such small portions withdrawn from such as larger batch do not, as a general rule, perfectly express the average composition of the larger batch, despite every effort to avoid deviation by effective methods of mixing the ingredients.

In the U.S. patent to Walton, 2,773,040, granted December 4, 1956, to the assignee of the instant invention, there is described a satisfactory solution of this problem in so far as it pertains to distribution of the aluminum particles within the mixture, it having been discovered that effective and uniform distribution of the aluminum can be achieved by the use of particles of fairly uniform size ranging from 150 to 350 particles per gram. The present invention is concerned with the problem of securing efficient and uniform distribution of the aforesaid additional ingredients and of the alkaline agent, it having been



found that this problem cannot be solved as in the case of the aluminum particles by reduction of the particle size, owing to the tendency of the additional ingredients to segregate during mixing.

A difficulty commonly encountered in the actual use of composition of this kind, for instance in the production of heat for the purpose of opening clogged drains, is that unless care is exercised in properly proportioning the solid ingredients and the added water, a dense cake of solid material, commonly called a "caustic heel," is left in the drain. These caustic heels constitute the principal objection of those working in the plumbing field to the use of heat-liberating mixtures for relieving clogging in drains, the final condition being sometimes worse than the initial clogging.

Again, when using oxidizing agents, such as sodium nitrate, it is important that the agent should dissolve rapidly on the addition of water to the mixture in order that the nitrate ions may go into solution in the early stages of the reaction between the alkaline agent and the aluminum, so that the hydrogen released by the latter reaction may be converted into ammonia and other reduction compounds as quickly as it is formed.

In my copending application, Serial No. 678,551, filed August 16, 1957, and now abandoned, and entitled "Heat-Producing Compositions," I have described and claimed a composition and a method of preparing the same which is effective in overcoming the aforementioned difficulties and in achieving various other advantages. These results are attained, pursuant to the illustrative embodiment of the said copending application, by bringing together in solution the soluble ingredients of the mixture, evaporating the solution, and reducing the residue into any convenient particle size. It is pointed out that when this practice is followed, the solid ingredients other than aluminum are homogeneously distributed in the "fused" particles. The result is a far more effective distribution of the several solids in small samples withdrawn from a large batch, surprisingly increased rapidity of soluton of the fused particles when water is added to the mixture, and minimum formation of "caustic heels." Such heels as may be formed are loose and easily flushed from a drain, even when the amount of water added to the mixture is substantially less than that required to prevent the formation of heels when using compositions prepared by conventional methods, or compositions in which the amount of aluminum present is inadequate.

I have also discovered, in the course of commercial development of the invention, that a serious corrosion problem arises when evaporator units are employed to remove the water from the fused mixture. This problem may be solved by employing anhydrous caustic and raising the temperature of the mixture sufficiently to melt the caustic and the nitrate. Water-soluble inorganic salts employed as fillers in the formulation, such as sodium chloride, dissolve in the molten caustic. Upon cooling to solidify the melted ingredients, for instance by flaking, and reducing the particle size to an optimum value by crushing or grinding, particles in which the several ingredients are fused and in which homogeneous distribution of ingredients occurs are readily and inexpensively produced.

Alternatively, the invention may be practiced with the use of caustic soda solutions at various concentrations,

the caustic solution, sodium nitrate and sodium chloride being admixed and the temperature then raised sufficiently to melt the caustic and the sodium nitrate, whereupon the sodium chloride readily goes into solution in the molten mixture. In the course of heating to melt the caustic, water is, of course, driven off, and corrosion problems may be avoided by addition of the nitrate after removal of most or all of the water. It is thus apparent that the presence of water is not only unnecessary to the preparation of the fused mixture but may be in some respects detrimental. In any event, it will be appreciated that by raising the temperature sufficiently to melt the caustic and the nitrate, a completely homogeneous mixture of these compounds may be obtained whether the starting material is anhydrous or not.

Among the surprising advantages obtained by the practice of this invention are the following:

(1) The formation of "caustic heels" after addition of water to the mixture in the use of the composition may be altogether eliminated by appropriate selection of the particle size of the fused salts, this effect being especially noticeable in a composition which is deficient in aluminum content.

(2) Segregation of the several components of the composition is minimized, with the result that small quantities withdrawn from a container are highly uniform in composition, and uniform and consistent results are insured.

(3) Because segregation of the ingredients is minimized by the present method, the ingredients may be more accurately proportioned, whereby a reduction in the proportion of caustic, which is the most expensive component excepting aluminum, may be reduced.

(4) The reaction of the composition on addition of water, evidenced by development of temperatures higher than 100° C., is sustained over a longer period of time and is quiet, even in compositions employing an exceptionally high aluminum content.

(5) Foaming of the mixture in use is significantly reduced, even when an excessive amount of the composition is employed, or when the composition contains an excessive amount of aluminum.

(6) The uniformity of distribution of aluminum particles in small amounts withdrawn from a container is enhanced.

(7) Wider latitude in formulation of the composition is permissible without detriment to performance.

Experimental data show that the particle size of the fused salts plays an important part in the reaction and that the optimum particle size lies between 20 mesh and 40 mesh. In practice a range of particle size of this order is somewhat too narrow, and it is found that excellent results are obtained within the wider range of 10 mesh to 40 mesh, so long as the fractions above and below these limits are relatively small. By contrast, when the caustic and salts are mechanically admixed, best results are obtained with a particle size less than 40 mesh, caustic heels being formed when the average particle size is greater than 40 mesh. This suggests that larger particles tend to block the access of water and to prevent smooth, continuous, and complete chemical reaction in the use of the compositions in the intended manner.

It will be understood that the present invention does not contemplate the production of an essentially new heat-producing composition and is not concerned with the formulation of the composition, excepting only generally as hereinbefore indicated. On the contrary, the invention relates solely to the discovery of the outstanding advantages achieved when the soluble ingredients are processed as hereinbefore outlined, before admixture with the aluminum. The invention is thus broadly applicable to compositions of the type in which the principal heat-producing components are aluminum and an alkaline agent, and containing an oxidizing agent for reaction with evolved hydrogen, excepting only such compositions as contain additional agents functioning to impair substantially or to inhibit the heat-generating action of the alkali and aluminum. It will thus be appreciated that no limitation of the scope of the invention is intended by the formulations of the following specific examples, these being merely representative of preferred compositions to which the invention has been applied.

### *Example I*

Ninety-one pounds of a 50% aqueous solution of caustic soda were heated to drive off the water, after which 40 pounds of sodium nitrate and 10 pounds of sodium chloride were added to the caustic. The heating was continued until a temperature of 604° F. was reached. At this temperature the caustic and nitrate were melted and the sodium chloride dissolved in the molten mixture.

The mixture was then fed to a chilled flaking roll and the flaked material was ground to form discrete particles having an average size between 10 and 40 mesh. Then 4.1 pounds of aluminum particles, averaging in size 250 particles per gram, were mixed thoroughly with the caustic-salt particles.

On the addition of water to the resulting composition a well sustained quiet reaction was obtained, leaving no caustic heel and evolving a negligible amount of hydrogen.

Similar results were obtained by using caustic solutions at 12% and 73%, respectively, with the same weight of caustic (45.5 pounds), and by the use of anhydrous caustic.

The maximum temperature reached need only be sufficient to melt the caustic and nitrate, heating to higher temperatures being unnecessary and uneconomical.

### *Example II*

Using the method of Example I, and employing varying particle sizes of the fused particles of caustic, nitrate, and chloride, in admixture with less than the optimum amount of aluminum particles, the following data were obtained by addition of water to the mixture in the usual manner.

| Formula: | Percent |
|---|---|
| NaOH | 46.02 |
| $NaNO_3$ | 40.46 |
| NaCl | 10.12 |
| Aluminum (average size 250 particles per gram) | 3.00 |
| Oil (straw) | .4 |

| Particle Size (Mesh) | Temperature Rise, ° C. | Quiescent Zone (Inches) | Foam | Heel | Time at 100° C. or Above (Minutes) |
|---|---|---|---|---|---|
| −6 +8 | 83.5 | 2¼ | 0 | Large | 4 |
| −8 +10 | 80.5 | 2¼ | 0 | do | 2 |
| −10 +14 | 83.5 | 2⅛ | 0 | Slight | 5 |
| −14 +20 | 84.5 | 2 3/16 | 0 | 0 | 5 |
| −20 +40 | 88.0 | 1⅞ | 0 | 0 | 8 |
| −40 | 81.5 | 2⅛ | 0 | 0 | 2 |

It will be observed from this data that the size of the fused particles is a significant factor, the characteristics obtained within the range less than 20 mesh and greater than 40 mesh being distinctly superior. Thus the temperature rise was greater, the quiescent zone less, and the duration of the reaction was prolonged. It will be appreciated that this particle size range may be somewhat narrow in practice, and it is found that comparable results are obtained within the somewhat wider range of 10 to 40 mesh when the percentages above and below this range are small.

By contrast, when the same formula mixed mechanically is employed, the caustic and nitrate being ground and sized separately to the particle sizes indicated, the

following results were obtained by use of the composition in the usual manner:

| Particle Size (Mesh) | Temperature Rise, ° C. | Quiescent Zone (Inches) | Foam | Heel | Time at 100° C. or Above (Minutes) |
|---|---|---|---|---|---|
| −6 +10 | 85.0 | 1 5/16 | 0 | Large | 5¼ |
| −10 +14 | 81.5 | 1 5/16 | 0 | do | 3¾ |
| −14 +20 | 82.0 | 1 3/16 | 0 | do | 5½ |
| −20 +40 | 82.0 | 1 5/16 | 0 | do | 4½ |
| −40 | 85.0 | 1⅞ | 0 | 0 | 6 |

It is significant that with one exception the caustic heel was large; only when the particle size was less than 40 mesh did the heel disappear. It is apparent, therefore, that by using the fused salts a greater tolerance is permissible in the aluminum content. This is of outstanding importance inasmuch as a certain amount of segregation of aluminum in small batches, and resulting lack of uniformity of aluminum content of a withdrawn sample may be expected.

Using essentially the same proportionate amounts of caustic, nitrate and chloride, with an excessive quantity of aluminum (6%), the fused salts again gave excellent results, the temperature rise being 84° C., the duration of the reaction at 100° C. or higher being 6½ minutes, and no caustic heel being formed.

*Example III*

For the purpose of determining the effect of fusion of salts and variation in particle size on hydrogen evolution, compositions prepared in accordance with the procedure outlined in Example I were compared with a mechanical mix employing the formula currently used in the assignee's product which is widely distributed under the trade name "Drano." The following results were achieved:

| | Formulae | | | Standard, Percent |
|---|---|---|---|---|
| | I, Percent | II, Percent | III, Percent | |
| NaOH | 45.5 | 45.5 | 45.5 | 54.2 |
| $NaNO_3$ | 40.0 | 40.0 | 40.0 | 30.45 |
| NaCl | 10.0 | 10.0 | 10.0 | 10.85 |
| Aluminum | 4.1 | 4.1 | 4.1 | 4.1 |
| Oil | .4 | .4 | .4 | .4 |

| Condition | Formula I | Formula II | Formula III | Standard |
|---|---|---|---|---|
| Salts | Fused | Fused | Fused | Loose. |
| Particle size | −8+10 | −40 | As ground [1] | Indefinite. |
| Hydrogen Evolved | 2.09 ml | 1.68 ml | 1.78 ml | 8.9 ml. |

[1] This was constituted as follows:

| | Percent |
|---|---|
| −6 +8 Mesh | 10.20 |
| −8 +10 Mesh | 23.15 |
| −10 +14 Mesh | 17.65 |
| −14 +20 Mesh | 10.10 |
| −20 +40 Mesh | 13.40 |
| −40 Mesh | 25.50 |
| Total | 100.00 |

It will be noted that Formulae I, II and III employ a less amount of caustic with consequent substantial reduction in expense. Nevertheless the amount of hydrogen evolved is negligible as compared with the amount of hydrogen released by the standard mechanically mixed formulation.

It may be observed that in the customary use of the standard mechanically mixed composition by withdrawing a small sample from a container for each use, a range



of proportions as wide as the following may be expected, however thoroughly the ingredients are mixed:

| | Percent by weight |
|---|---|
| Caustic soda | 40 to 67 |
| Sodium chloride | 6 to 25 |
| Sodium nitrate | 20 to 40 |
| Aluminum | 2 to 8 |

While variation within these ranges may be tolerated, variation of this order in a widely distributed commercial product is obviously undesirable and is avoided by the practice of the instant invention, except as to aluminum, and greater tolerance to aluminum variation is possible.

While the size of the aluminum particles is preferably that proposed in the patent to Walton, 2,773,040 aforementioned, averaging from about 150 to about 350 particles per gram, and preferably from about 225 to about 275 particles per gram, somewhat larger particles may be employed when the instant invention is practiced, for example, 100 to 200 particles per gram. Preferably an aluminum alloy of the composition described in the U.S. patent to Walton, 2,816,012, granted December 10, 1957, is used. It will be appreciated, however, that the invention is not concerned with these aspects of the composition, but is addressed to a novel method of bonding or fusing the several water-soluble ingredients and with the homogeneous product thereby obtained.

As hereinbefore explained, the primary function of the sodium nitrate is to combine with the hydrogen released in the reaction between the alkaline agents, ordinarily sodium or potassium hydroxide, and the aluminum. Hydrogen is generated principally in the early stages of the reaction, and it is thus important that when water is added to the composition, the sodium nitrate be dissolved as quickly and completely as possible in order to obtain conversion of a maximum amount of evolved hydrogen to ammonia and other reduction compounds. It is believed that when the mixture of salts, caustic soda, sodium nitrate, and sodium chloride is sufficiently intimate, as when the present invention is employed, the mixture exhibits both a faster rate of solution and a greater final solubility than is the case when the salts are separately dissolved, each exerting a favorable solubility effect on the others.

It is desired to emphasize the obvious fact that my invention is applicable broadly to the preparation of compositions developing heat on the addition of water, and containing a mixture of aluminum, alkaline agent, and an oxidizing agent, and containing such other optional ingredients as are commonly empolyed in such compositions, for instance a small amount of straw oil.

Obviously sodium nitrate is not the only water-soluble oxidizing agent which may be employed in the instant invention. Nevertheless, it is the preferred agent from the standpoint both of effective performance and economy. Similarly, while the filler serves merely as a diluent and its nature is therefore relatively unimportant, it is preferably water-soluble for obvious reasons, and sodium chloride is inexpensive and quite satisfactory. The purpose of the instant invention is not the development of a new formulation for heat-producing compositions of the type indicated, but a method of combining several conventional ingredients in such manner as to minimize segregation with resultant clear improvement in uniformity of both the composition and of the results achieved in use.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. A method of preparing in dry particulate form a composition liberating heat when added to water, said composition consisting essentially by weight of 2–8% aluminum particles of a size averaging from about 100–350 particles per gram, 40–67% alkali metal hydroxide and 20–40% by weight sodium nitrate, in intimate admixture, said alkali metal hydroxide being present in an amount at least twice the theoretical amount required

for combination with the aluminum, and said sodium nitrate being present in amount sufficient to react with hydrogen released in the reaction of aluminum and hydroxide, which method includes the steps of preparing a substantially water-free molten mixture of said hydroxide and nitrate, solidifying the mixture by cooling, subdividing the solidified mixture into discrete particles having an average size between 10 and 40 mesh, and admixing the last-named particles with said aluminum particles to form said composition.

2. The method of claim 1 wherein said molten mixture is prepared by heating said hydroxide and nitrate to melt the same.

3. The method of claim 1 wherein said molten mixture is prepared by evaporating water from an aqueous solution of said hydroxide until substantially water-free, thereafter adding said nitrate, and heating said hydroxide and nitrate until melted.



4. The method of claim 1 wherein said composition contains in addition to said hydroxide, nitrate, and aluminum particles 6–25% by weight of sodium chloride and including the further step of dissolving said chloride in said molten mixture of hydroxide and nitrate.

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