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PROCESS FOR IMPROVING THE PROPERTIES OF A COMPACTED FORM OF SODIUM CYANIDE CRYSTALS

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Fig. 1

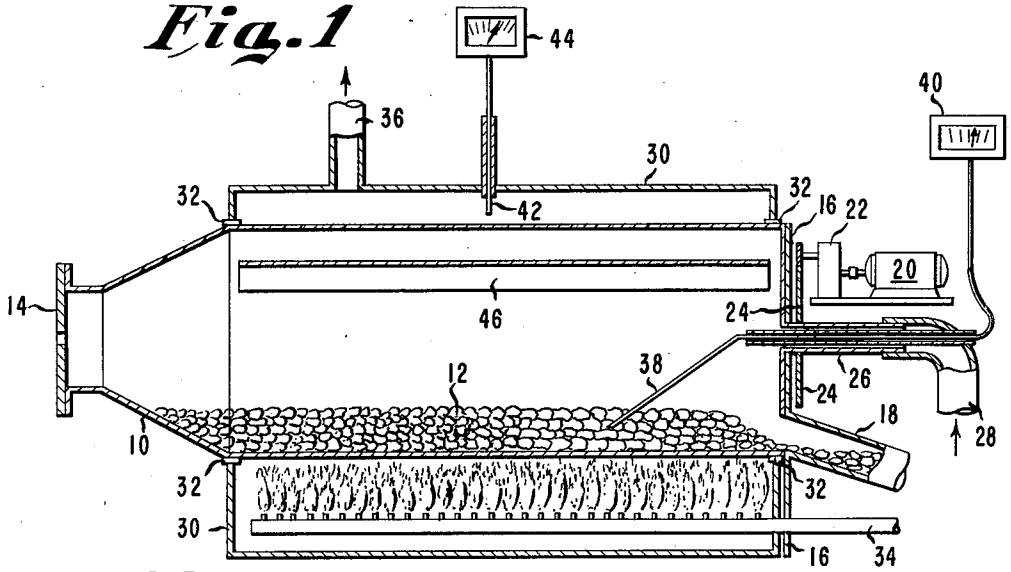
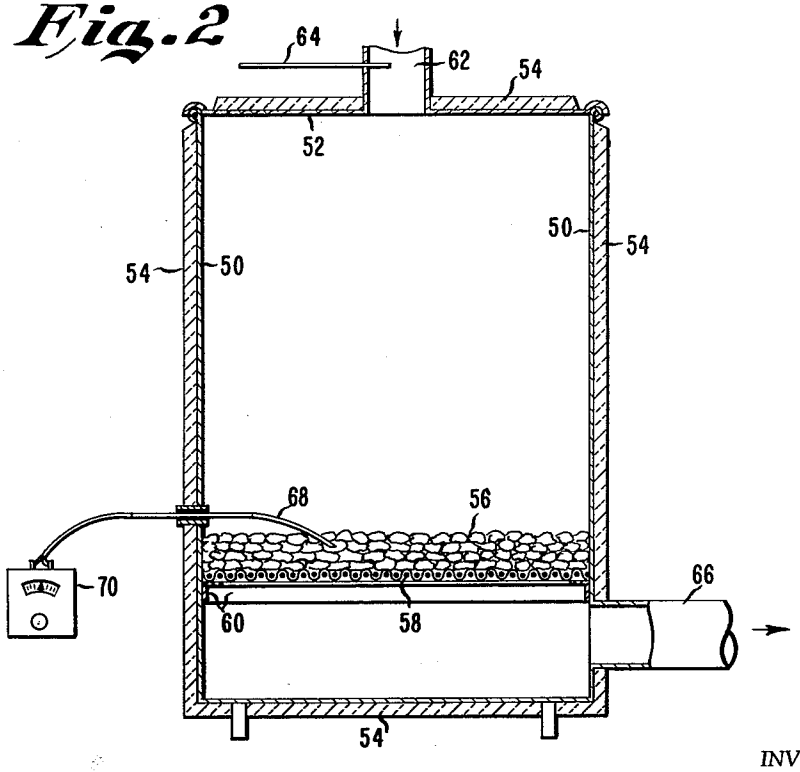


Fig. 2



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PROCESS FOR IMPROVING THE PROPERTIES OF A COMPACTED FORM OF SODIUM CYANIDE CRYSTALS

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2 Claims. (Cl. 23—79)

This application is a continuation-in-part of application Serial No. 716,501, filed February 20, 1958, now abandoned.

This invention relates to compacted forms of sodium cyanide crystals, and is more particularly concerned with a heat-treating process for improving briquettes which have been formed by pressing together finely divided sodium cyanide crystals, and with the improved briquettes produced by said process.

A large amount of sodium cyanide is supplied for industrial use in molded forms. Such molded forms are greatly preferred for general use because of the ease and safety in handling in comparison with finely divided forms which are dusty and relatively hazardous. Sodium cyanide produced by the dry Castner process is obtained directly in the molten state and is, therefore, cast into a molded form. Customarily, this form is of spherical shape weighing about one ounce and referred to as "eggs." Sodium cyanide produced by the newer wet process is recovered from an aqueous solution by crystallization and drying and obtained in the form of finely divided crystals. It has not been found practical to melt and cast these crystals into molded forms such as eggs due to the extra cost involved and because product darkening and product decomposition occur. Instead, the substantially dry crystals are pressed into a compacted form, usually as the finely divided crystals come from a dryer at a temperature of about 140–160° C. Obviously, the crystals might be pressed into forms of many different shapes and sizes but customarily is pressed into a pillow shape weighing approximately one ounce and referred to as "briquettes." Although the present invention concerning the improvement of compacted forms of sodium cyanide crystals is applicable to compacted forms of sodium cyanide crystals of any shape or size, as a matter of convenience it will be described hereinafter in connection with briquettes.

Although briquettes formed as above described can currently be more economically produced than cast eggs, unfortunately, they frequently give unsatisfactory results in processes for which cast eggs have been quite satisfactory. It has now been found that the difficulty usually encountered in using briquettes instead of cast eggs results from absorption of moisture upon exposure to the atmosphere. This is particularly the case in the metal treating industry where sodium cyanide additions are made to fused carburizing and nitriding baths. When the moisture content of the sodium cyanide is as high as 0.5% by weight, excessive flame and sputtering occur and a layer of foam forms on the surface of the molten bath, frequently overflowing the pot and spilling into the heating elements of the furnace. This is, of course, undesirable and hazardous. Even though the sodium cyanide briquettes are dry when shipped to the user, most shops engaged in this operation use from the same container over a long enough time for an objectionable amount of moisture to be absorbed from the shop atmosphere. Also, absorbed moisture is often objectionable when using sodium cyanide as a raw material in chemical syntheses because the yields are adversely affected by the presence of moisture. Moreover, since the briquettes are formed by merely pressing together fine crystals of sodium cyanide, said briquettes

have limited mechanical strength and are considerably more fragile in use than cast eggs in which the sodium cyanide is fused.

It is an object of this invention, therefore, to provide a process, for improving the properties of sodium cyanide briquettes. Another object is to provide briquettes which have low moisture absorption characteristics. Another object is to provide briquettes suitable for use in fused metal-treating baths. Another object is to provide briquettes of improved mechanical strength and appearance. A still further object is to provide briquetes in which the amount of sodium formate present as an impurity is minimized.

In accordance with the present invention, it has been found that the properties of sodium cyanide briquettes are greatly improved by heating for at least 15 minutes at temperatures in the range of 350–450° C., with sufficient free alkali metal hydroxide present in the sodium cyanide to provide 0.1–1.0% by weight in the product, the briquettes being cooled thereafter without further treatment. The treated briquettes are characterized in having a low moisture absorption tendency and are quite suitable for use in fused metal-treating baths. The treatment makes the briquettes significantly harder and more resistant to breakage or formation of powder. The appearance of the briquette is also improved, especially by being markedly whitened to a uniform pure white.

The process will be described with reference to sodium cyanide briquettes, but is also useful for improving the properties of other compression molded alkali metal cyanides, such as potassium cyanide. The improvement in properties will be indicated principally by reference to the effect on moisture absorption and the effect on suitability for use in fused baths for metal heat-treating purposes, since numerical comparisons of the effect of the treatment are readily made. However, significant improvements in the other properties mentioned above are also obtained. Moreover, it has been found that the process of the invention has a significant effect in reducing the amount of sodium formate present so that the treated briquettes are characterized in exhibiting a much lower content of sodium formate than the untreated briquettes. Sodium formate is invariably present in briquetes formed from sodium cyanide crystals produced by the wet process since this material is unavoidably formed as a result of the reaction between water and sodium cyanide, and is usually present in amounts in excess of 0.3% by weight in the initially formed briquettes. Besides lowering the purity of the product, sodium formate is found to be a very objectionable impurity since it has been found to contribute in itself to flaming and foaming when briquetes are added to heat-treating baths and, in addition, is found to adversely affect yields in various chemical syntheses when sodium cyanide is used as a reactant material. For briquettes used in heat-treating baths, it has now been found highly preferable to maintain the content of sodium formate below 0.2% by weight and contents of sodium formate below this level may be readily obtained in briquettes treated by the process of the present invention.

Heating the briquettes in the temperature range of 350–450° C. is quite critical in order to lower the moisture absorption characteristics and to effect the other stated improvements in properties. The briquettes may be heated in any convenient way for at least 15 minutes in this temperature range as in the presence of air at substantially atmospheric pressure, and are then cooled or allowed to cool. Since moisture reacts with sodium cyanide to form sodium formate and ammonia at an increasingly rapid rate as the temperature is raised, it is preferable that the briquettes be substantially dry and be surrounded by a substantially dry atmosphere during the

heating and cooling steps. Briquettes which contain appreciable moisture should first be dried at temperatures below about 200° C. The briquettes can be heated in a closed container or in a stream of hot air or other inert gas. The process is most conveniently carried out with a continuous rotary oven which is indirectly heated or supplied with hot air to heat the briquettes to 350—450° C. as the briquettes are fed through the heating machine. Atmospheric air heated to a temperature above 350° C., preferably 400–450° C., is suitable for this purpose without preliminary drying.

A minimum of 0.1% by weight sodium hydroxide or other alkali metal hydroxide must be present in the briquettes throughout the treatment to prevent darkening. For briquettes that are to be used to form aqueous solutions 0.3% by weight of alkali metal hydroxide is preferred in order to avoid hydrolysis and formation of cyanide polymers, etc. On the other hand, the purity of the product should not be lowered by the presence of more than about 1.0% by weight of sodium hydroxide, and it is generally preferable to have about 0.3–0.6% by weight present in the final product. It has been found in accordance with the present invention that a larger amount of hydroxide must be provided at the start of the process because of the sodium formate which is present in the untreated briquette, due to the following reaction which apparently occurs during the heating within the 350–450° C. temperature range:

$$NaOH+HCOONa \rightarrow Na_2CO_3+H_2$$

In addition to the sodium formate initially present as an impurity, additional formate may be formed by any moisture present which reacts with the sodium cyanide. The net effect of any moisture present in the untreated briquette, therefore, is as follows:

$$NaOH+2H_2O+NaCN \rightarrow Na_2CO_3+H_2+NH_3$$

The percent by weight of sodium hydroxide which will be used up by these two reactions is approximately (40/58) (percent by weight sodium formate present) plus (40/36) (percent by weight moisture present). However, the amount of sodium hydroxide actually used up need not be estimated in this way, since it can easily be determined by trial under the specific conditions to be employed.

The reason for the improvement achieved by the process of this invention is not completely understood but is believed to result from crystal growth which in turn reduces the degree of porosity of the briquette. While the untreated briquette is of stable form and seems solid, pressed briquettes can be shown to be relatively porous by tests with wet dyes, by water absorption rates or by treatment with carbon dioxide. At 350–450° C. temperature of the invention which is well below the melting point for sodium cyanide, namely, 560° C., the fine crystals apparently grow together to reduce the porosity and, surprisingly, while remaining free of fused sodium cyanide, the treated briquettes gain significant mechanical strength approaching the strength of cast eggs containing fused sodium cyanide throughout the molded form. As a result of the treatment, the moisture absorption of briquettes is readily reduced to less than one-half that of untreated briquettes upon exposure to common atmospheric conditions. As shown in the subsequent examples, the moisture absorption of treated briquettes is less than 0.3% by weight and, depending upon the conditions, may even be less than 0.1% by weight. The absorption inside the briquettes is most sharply reduced. Moisture absorbed on the outside of briquettes is driven off without difficulty when briquettes are added to a fused heat-treating bath, whereas moisture absorbed within the briquettes has been found to cause objectionable foaming.

Specific embodiments of the invention will now be described with reference to the figures of the drawing wherein FIGURE 1 is a sectional representation of a

rotary apparatus suitable for continuous processing of briquettes in accordance with the invention, the section being taken along the axis, and FIGURE 2 illustrates an apparatus, likewise in section, which is suitable for batch operations.

The apparatus illustrated in FIGURE 1 is an indirectly heated, rotary shell heating machine of conventional type suitable for continuous operation. A horizontal rotating shell **10** of generally cylindrical shape contains the briquettes **12** while they are heated. The briquettes are fed into the shell at one end through the opening in end cover **14**. In continuous operation, they pass along the length of the shell and are removed through the opening in the other end cover **16** after sufficient treatment, passing through chute **18** to customary handling equipment. Cooling by natural heat transfer is usually preferable, although means for more rapid cooling can be provided. The shell is rotated by motor **20** acting through reducing mechanism **22** and gear **24** mounted on hollow axle **26** attached to the shell. Duct **28** is provided to feed air into the shell through the hollow axle, if a circulation of air is desired, e.g., for direct heating of the briquettes with hot air. When air is supplied in this way, it passes through the shell and out through the opening in cover **14** at the opposite end.

The shell is surrounded by a housing **30** which supports the shell on bearings **32**, indicated at each end of the shell. A gas burner **34** is provided for generating hot flue gases within the housing. The hot flue gases pass around the autside of the shell and leave the housing through duct **36**. Obviously, other means for indirect heating of the briquettes can be used instead of the burner **34**, or indirect heating can be omitted if the briquettes are heated by direct contact with hot air introduced through duct **28**. The temperature of the briquettes is measured by a thermocouple **38** connected to a recorder **40**. The temperature of the hot gases within the housing is measured by thermocouple **42** connected to recorder **44**. Flights or paddles **46**, mounted on the inside of the shell, improve the tumbling action in order to heat the briquettes more effectively.

All percentages stated in the following examples are percents by weight unless otherwise indicated.

EXAMPLE 1

Briquettes, each weighing approximately 1 ounce, were heated in an apparatus of the type disclosed above. A 28-inch diameter stainless steel shell, 46 inches long, was used. Two flights were provided to give a mild tumbling action. The shell was rotated at 3 revolutions per minute. A gas burner was used to raise the temperature of the flue gas leaving the housing to about 400° C. The briquettes had previously been dried at 180° C. to 0.01% moisture and analyzed 97.3% NaCN, 0.97% NaOH, 0.97% Na_2CO_3 and 0.28% HCOONa. After heating for 90 minutes the temperature of the briquettes was 300° C. and a portion was removed. The heating was continued for an additional 40 minutes, to heat the remaining briquettes at about 350° C. for 15 minutes, and they were then removed. The briquettes were cooled by natural heat transfer and analyzed for moisture content. The briquettes were then exposed to an atmosphere of 62% relative humidity at 77° F. for 4.5 hours, and then analyzed for moisture content again and tested by adding 10 pounds to the pot of an industrial heat-treating bath at 1480–1500° F. The results of the analyses and tests are shown in Table I.

EXAMPLE 2

Example 1 was repeated but with the gas burner adjusted to raise the temperature of the flue gas to about 450° C. After heating for 90 minutes the temperature of the briquettes was about 350° C. The heating was continued for 15 minutes, during which time the briquettes were at 350–370° C., and a portion was removed.

The heating was then continued for an additional 45 minutes to raise the temperature of the briquettes to 400° C. The briquettes were then cooled, analyzed for moisture, exposed to an atmosphere of 62% relative humidity for 4.5 hours, analyzed again for moisture and tested as in Example 1. The results are shown in Table I.

Table I

EFFECT OF HEATING BRIQUETTES TO INDICATED TEMPERATURES

° C. Temp.	Percent NaCN	Percent NaOH	Percent Na_2CO_3	Percent HCOONa	Percent H_2O After Exposure	Performance in heat-treating bath
300	97.2	0.81	1.05	0.24	0.68	6 inches of foam (overflowed pot).
350	97.0	0.65	1.39	0.11	0.25	1½ inches of foam.
370	96.9	0.53	1.57	0.19	0.24	¾ inch of foam.
400	96.8	0.46	1.71	0.08	0.23	No foam.

The treated briquettes were pure white in each instance. The moisture content of the treated briquettes before exposure to the moist atmosphere was below 0.05% by weight for each run reported in Table I.

The above results show that heating to 350–400° C. for at least 15 minutes remarkably reduced the moisture absorption, and the amount of foam produced in the heat-treating bath, in comparison with merely heating to 300° C. The performance of briquettes heated at 350° C. for 15 minutes was equal to that of cast eggs in heat-treating operations, and that of the samples heated to 370–400° C. was even more satisfactory. The comparison sample, heated only to 300° C., absorbed nearly 3 times as much moisture in the short exposure to atmosphere at typical humidity-temperature conditions and was quite unsatisfactory for heat-treatment purposes. This clearly indicates the criticality of operating the process of the invention at a temperature of at least 350° C. in order to improve the properties of briquettes.

From tests made similar to Example 1 and 2, it was found that temperatures above 450° C. are undesirable since discoloration of the briquettes occur above this temperature. Furthermore, it is an important advantage to remain well below the melting point of sodium cyanide to avoid the softening or the melting of the briquettes to a point where they stick or adhere to one another.

Briquettes can also be processed satisfactorily in the stationary direct heating oven shown in FIGURE 2. A cylindrical metal container **50** is provided with a tight fitting lid **52**, both being covered with insulation **54**. The briquettes **56** are supported on a false bottom formed by 8 mesh screen **58** resting on angle iron supports **60**. Hot air is supplied to the container through duct **62** in the lid **52**. A thermometer **64** is provided in this duct to measure the entering air tempearture. The air passes downward through the briquettes into the space below the false bottom and is withdrawn through duct **66** in the bottom side of the container. The temperature of the briquettes is measured with a thermocouple **68** connected to a recorder **70**.

EXAMPLE 3

Briquettes of the 1-ounce size were heated for 15 minutes at 450° C. in the oven disclosed above with reference to FIGURE 2. The starting briquettes, which had previously been dried at 180° C., analyzed 97.1% NaCN, 0.55% NaOH, 1.24% Na_2CO_3, 0.37% HCOONa, 0.12% NaCNO and 0.7 p.p.m. Na_2S. After heating at 450° C. the briquettes were pure white and analyzed 96.7% NaCN, 0.10% NaOH, 2.41% Na_2CO_3, 0.09% HCOONa, 0.09% NaCNO, and 0.6 p.p.m. Na_2S. When exposed to an atmosphere of 65% relative humidity at 77° F. for 2.5 hours, the treated briquettes absorbed only 0.07% moisture. By comparison, the initial briquettes absorbed 0.48% moisture in this test. Both the treated and the initial briquettes had a moisture content below 0.05% before the exposure test. The treated briquettes after exposure to the moisture test were entirely satisfactory when tested for heat treatment use. There was no foam when 9 pounds were added to an industral heat-treating bath at a temperature of 1520° F. On the other hand, the untreated briquettes were completely unsatisfactory for this purpose after the short exposure to 65% relative humidity. Addition of only 5 pounds to the bath produced 4 inches of foam and caused the pot containing the treating bath to overflow.

It is preferable to provide for uniform contact of the briquettes with hot air, by tumbling the briquettes as in Examples 1 and 2, or by forced flow of hot air through the briquettes as in Example 3, or in both ways, since the briquettes will then be heated more effectively to the required temperature range. However, the briquettes can also be heated in a stationary closed container.

EXAMPLE 4

Briquettes were processed as in Example 3 except that the briquettes were in a closed container placed within the oven and were heated for various times at 400° C. The corresponding analyses were as follows:

Time in Minutes at 400° C.	Percent NaCN	Percent NaOH	Percent Na_2CO_3	Percent HCOONa	Percent H_2O After Exposure
Start	97.3	0.38	1.25	0.29	0.41
15	97.3	0.14	1.52	0.19	0.08
30	97.3	0.10	1.69	0.08	0.11
45	97.6	0.13	1.72	0.08	0.05

The briquettes were pure white after heating.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

I claim:

1. A process for improving the properties of a compacted form of sodium cyanide crystals of at least 96.0% by weight purity and containing at least 0.1% by weight of alkali metal hydroxide which comprises heating said compacted form for at least 15 minutes at a temperature below the fusion point within the range of from 350–450° C., and then cooling said compacted form at the conclusion of said treatment; the amount of said alkali metal hydroxide being sufficient to provide 0.1–1.0% by weight in said compacted form after said treatment.

2. A process for improving the properties of a compacted form of sodium cyanide crystals of at least 96.0% by weight purity and containing at least 0.3% by weight of alkali metal hydroxide, which comprises heating said compacted form for at least 15 minutes at a temperature below the fusion point within the range of from 350–450° C., and then cooling said compacted form at the conclusion of said treatment; the amount of said alkali metal hydroxide being sufficient to provide 0.3–0.6% by weight in said compacted form after said treatment.

References Cited by the Examiner

UNITED STATES PATENTS

859,482	7/07	Bueb	23—84 X
912,538	2/09	Bueb	23—79 X
1,262,057	4/18	Kaufman	23—79
2,365,417	12/44	Kusman	23—79
2,710,788	6/55	Copelin	23—84
2,773,752	12/56	Kremer et al.	23—84 X

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