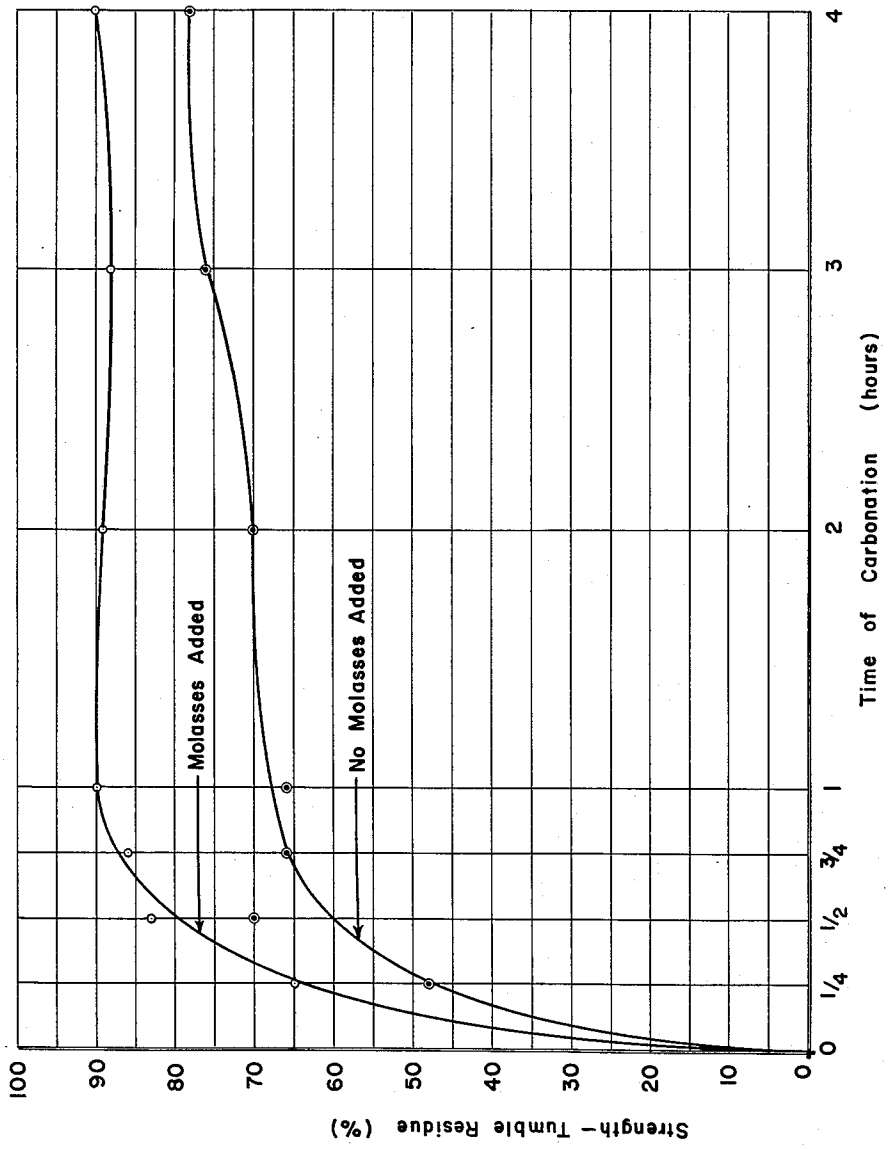
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LUMP ORES AND METHODS OF PRODUCING THEM

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LUMP ORES AND METHODS OF PRODUCING THEM

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This invention relates to lump ores and to methods of producing them and particularly to a lump ore and method of producing such an ore from finely divided materials containing metals in the metallic state, as metallic compounds such as oxides or mixtures thereof. The invention is particularly adapted to the production of lump iron ores from finely divided iron ores, blast furnace flue dust and other sources of iron and iron compounds which are available in a fine state of subdivision.

This application is an improvement over the lump ores and methods of producing them disclosed in copending application Serial No. 470,523, filed November 22, 1954, in the name of Charles W. Amberg and assigned to the same assignee, now Patent No. 2,844,457, granted July 22, 1958.

In the case of iron ore, for example, natural reserves of high grade lump ores are rapidly being depleted by selective mining. It has been increasingly necessary to utilize the more finely divided high grade ores as well as to turn to low grade ores which must be beneficiated. In using such ores it is not uncommon to find them in size ranges such that they pass through a 200 to 325 mesh. In addition to these finely divided natural ores there are large quantities of blast furnace flue dust, fine scale, and similar other sources of iron and iron compounds available in the finely divided state for use in iron and steel-making processes. However, these materials, because of their fineness, tend to fuse and bridge over or to be flushed out with the early slag before accomplishing their metallurgical function in the open hearth steel-making furnace or to be carried out through the top of the blast furnace in iron making and are not suitable in their naturally occurring condition for use in open-hearth steel-making furnaces or in blast furnaces. In order to take advantage of these materials, it has been the practice to take these finely divided materials and either sinter, pelletize or nodulize them by heating to high temperatures or by bonding them together with hydraulic cement. All of these practices are relatively expensive and in some instances are undesirable because of the increased amounts of impurities such as silica and alumina which are introduced into the ore by the bonding practice.

I have discovered an improved lump ore product produced from such finely divided materials and a method of producing it. The lump ores produced according to my invention are free from the objections common to the presently used ores produced by sintering, pelletizing and nodulizing finely divided materials. The lump ore of this invention has the desirable thermal and chemical characteristics of natural lump ore, and has the strength and resistance to crushing characteristic of natural lump ores. The lump ore of this invention is, moreover, free from undesirable added impurities, contains bonding materials similar to the fluxing materials normally used in metallurgical practices and may be formed of blended or mixed iron-containing materials.

Amberg application Serial No. 470,523 previously referred to provides a method of forming lump ore products from finely divided metal containing material by bonding the materials together with an alkaline earth carbonate and formed by mixing the finely divided metal containing material with an oxide or hydroxide of calcium, mixed calcium and magnesium in the presence of mixture within

specific limits forming the lumps and treating them with carbonic acid gas. This practice produces a lump ore product having highly desirable characteristics and being superior to anything previously available. I have found, however, that the product of the Amberg application can be significantly improved particularly when finely divided high calcium oxides or hydroxides are used in the mixture. I have discovered that the addition of solubilizing agents for calcium and magnesium such as soluble carbohydrates (sugars, sugar containing materials and starches), Versene (the sodium salt of ethylene-diamene tetra acetic acid [see Handbook of Material Trade Names, Zimmerman and Lavine, 1953 ed.]) and like agents to the mixture prior to carbonation will significantly improve the resistance of the lump ores to crushing and disintegration under impact and at the same time markedly increase the rate of carbonation. I have found that the addition of small amounts of certain solubilizing agents for calcium and magnesium oxides and hydroxides, particularly in the range .025 to 2% by weight will more than double the resistance of the lump ores to physical attrition. The invention can perhaps best be explained by reference to the following examples which show the significance of the practice according to my invention:

EXAMPLE I

A low ignition hematite ore from Venezuela commonly designated as "Venz Lilo Ore" was mixed with 3.5% of dolomitic monohydrated lime known in the trade as "Ohio Superfine." This material is 99% minus 325 mesh. To this mixture was added 9% by weight of water on the basis of the weight of the ore. This mixture was divided into four parts. Into one part was added 0.20% calcium chloride. To another part was added 0.35% blackstrap molasses. To the fourth part was added .35% blackstrap molasses and .20% calcium chloride. The four parts were briquetted and were subjected to an atmosphere of 100% carbon dioxide for 2½ hours. The resulting briquets were tumbled in an A.S.T.M. coke tumbler and the average percentage of residue on a .371 mesh after 50 revolutions was determined. The results appear in Table I.

Table I

Material	Percent by Weight	Average Tumble Test
Venz Lilo Ore	100	37
Ohio Superfine	3.5	
Water	9	
Venz Lilo Ore	100	55
Ohio Superfine	3.5	
Calcium Chloride	0.2	
Water	9	
Venz Lilo Ore	100	81
Ohio Superfine	3.5	
Blackstrap Molasses	0.35	
Water	9	
Venz Lilo Ore	100	90
Ohio Superfine	3.5	
Blackstrap Molasses	0.35	
Calcium Chloride	0.2	
Water	9	

EXAMPLE II

The same Venezuelan ore as in Example I was mixed with 5% of the same lime as in Example I and 9% water by weight on the weight of the ore. This mixture was divided into six parts. To one part was added .2% calcium chloride. To the next part was added .5% blackstrap molasses. To the next part was added .5% blackstrap molasses and .2% calcium chloride. To the fourth part was added .25% sucrose. To the fifth part was added .25% sucrose and .2% calcium chloride. All percentages are by weight on the weight of the ore. The six parts were briquetted and treated with an atmosphere of 100% carbon dioxide for 2½ hours. After carbonation, the

briquets were tumbled as in Example I. The results are shown in Table II.

Table II

Material	Percent by Weight	Average Tumble Test
Venz Lilo Ore	100	
Ohio Superfine	5	66
Water	9	
Venz Lilo Ore	100	
Ohio Superfine	5	
Calcium Chloride	0.2	72
Water	9	
Venz Lilo Ore	100	
Ohio Superfine	5	
Blackstrap Molasses	0.5	90
Water	9	
Venz Lilo Ore	100	
Ohio Superfine	5	
Blackstrap Molasses	0.5	
Calcium Chloride	0.2	92
Water	9	
Venz Lilo Ore	100	
Ohio Superfine	5	
Sucrose	0.25	88
Water	9	
Venz Lilo Ore	100	
Ohio Superfine	5	
Sucrose	0.25	92
Calcium Chloride	0.2	
Water	9	

EXAMPLE III

The same Venezuelan ore as in Example I was mixed with 3½% by weight on the weight of the ore of a dolomitic monohydrated lime from Plymouth Meeting, Pennsylvania, known in the trade as "Corson Regular." 88–92% of this material is minus 325 mesh. To this was added 9% water. The mixture was divided into four portions. To one portion was added .2% calcium chloride. To the second portion was added .35% blackstrap molasses. To the third portion was added .35% blackstrap molasses and .2% calcium chloride. The four portions were briquetted and subjected to an atmosphere of 100% carbon dioxide for 2½ hours. The resulting briquets were tumbled as in Example I. The results appear in Table III.

Table III

Material	Percent by Weight	Average Tumble Test
Venz Lilo Ore	100	
Corson Regular	3.5	38
Water	9	
Venz Lilo Ore	100	
Corson Regular	3.5	
Calcium Chloride	0.2	42
Water	9	
Venz Lilo Ore	100	
Corson Regular	3.5	
Blackstrap Molasses	0.35	71
Water	9	
Venz Lilo Ore	100	
Corson Regular	3.5	
Blackstrap Molasses	0.35	85
Calcium Chloride	0.2	
Water	9	

EXAMPLE IV

The same Venezuelan ore as in Example I was mixed with 5% by weight of Corson Regular lime and 9% water. The mixture was divided into eleven portions. To one portion was added .2% calcium chloride. To the other portion was added .25% blackstrap molasses. To the third portion was added .25% blackstrap molasses and .2% calcium chloride. To the fourth portion was added .5% blackstrap molasses. To the fifth portion was added .1% sucrose. To the sixth portion was added .1% sucrose and .2% calcium chloride. To the seventh portion was added .25% maltose. To the eighth portion was added .25% maltose and .2% calcium chloride. To the ninth portion was added .25% dextrose. To the tenth portion was added .25% dextrose and .2% calcium chloride. These mixtures were all briquetted, carbonated and

tumbled in the same manner as Example I. The tumble test results appear in Table IV.

Table IV

Material	Percent by Weight	Average Tumble Test
Venz Lilo Ore	100	
Corson Regular	5	57
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Calcium Chloride	0.2	63
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Blackstrap Molasses	0.25	73
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Blackstrap Molasses	0.25	
Calcium Chloride	0.2	81
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Sucrose	0.1	78
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Sucrose	0.1	
Calcium Chloride	0.2	83
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Maltose	0.25	59
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Maltose	0.25	
Calcium Chloride	0.2	74
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Dextrose	0.25	61
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Dextrose	0.25	
Calcium Chloride	0.2	76
Water	9	

This basic mixture of Venz Lilo Ore, Corson Regular and water was also varied with from 0.25% to 2% blackstrap molasses with almost uniform results. The same uniform good results were obtained by varying the amount of sucrose from 0.1% to 1%, maltose from 0.25% to 2% and dextrose from 0.25% to 2%.

EXAMPLE V

The same Venezuelan ore as Example I was mixed with 5% by weight of a high calcium hydrated lime from Newton, New Jersey, called in the trade "Limecrest Hydrate." This material is 84% minus 325 mesh. 9% water was added to the mixture. The mixture was then divided into two parts. To one part was added .20% calcium chloride. To the second part was added .50% sucrose and .20% calcium chloride. The mixture was briquetted, carbonated and tumbled as in Example I. The results of the tumble test are shown in Table V.

Table V

Material	Percent by Weight	Average Tumble Test
Venz Lilo Ore	100	
Limecrest Hydrate	5	19
Calcium Chloride	0.2	
Water	9	
Venz Lilo Ore	100	
Limecrest Hydrate	5	
Sucrose	0.5	65
Calcium Chloride	0.2	
Water	9	

EXAMPLE VI

The same Venezuelan ore as Example I was mixed with 5% by weight of a high calcium hydrated lime from Bellefonte, Pennsylvania, called in the trade "National Gypsum #26F." This material is 98% minus 325 mesh.

9% water was added to the mixture. The mixture was then divided into three parts. To one part was added .2% calcium chloride. To the second part was added .1% blackstrap molasses and .2% calcium chloride. The mixtures were briquetted, carbonated and tumbled as in Example I. The results of the tumble test are shown in Table VI.

Table VI

Material	Percent by Weight	Average Tumble Test
Venz Lilo Ore	100	
National Gypsum #26F	5	
Calcium Chloride	0.2	37
Water	9	
Venz Lilo Ore	100	
National Gypsum #26F	5	
Calcium Chloride	0.2	61
Blackstrap Molasses	1	
Water	9	

Several briquettes from the second portion were tumbled without carbonation and the tumble test reading was only 8.

EXAMPLE VII

The same Venezuelan ore as in Example I was mixed with 5% by weight of Corson Regular lime and 9% water. The mixture was divided into four portions. To each portion was added .2% calcium chloride. To one portion was added .25% corn syrup. To the second portion was added .5% corn syrup. To the third portion was added .35% corn starch. To the fourth portion was added .65% corn starch. These mixtures were all briquetted, carbonated and tumbled in the same manner as in Example I. The tumble test results appear in Table VII.

Table VII

Material	Percent by Weight	Average Tumble Test
Venz Lilo Ore	100	
Corson Regular	5	
Corn Syrup	0.25	88
Calcium Chloride	0.2	
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Corn Syrup	0.5	89
Calcium Chloride	0.2	
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Corn Starch	0.35	68
Calcium Chloride	0.2	
Water	9	
Venz Lilo Ore	100	
Corson Regular	5	
Corn Starch	0.65	72
Calcium Chloride	0.2	
Water	9	

EXAMPLE VIII

Liberian Ore fines (magnetite) was mixed with 3½% by weight on the weight of the ore of a different dolomitic monohydrated lime from Plymouth Meeting, Pennsylvania, and known in the trade as "Corson Regular." 88–92% of this material is minus 325 mesh. To this was added 7% water. The mixture was divided into two portions. To one portion was added .2% calcium chloride. To the second portion was added .35% blackstrap molasses and .2% calcium chloride. The two portions were briquetted and subjected to an atmosphere of 100% carbon dioxide for 2½ hours. The resulting briquettes were tumbled as in Example I. The results appear in Table VIII.

Table VIII

Material	Percent by Weight	Average Tumble Test
Liberian Ore Fines	100	
Corson Regular	3.5	38
Calcium Chloride	0.2	
Water	7	
Liberian Ore Fines	100	
Corson Regular	3.5	
Blackstrap Molasses	0.35	78
Calcium Chloride	0.2	
Water	7	

EXAMPLE IX

The same Liberian Ore fines of Example VIII were mixed with 5% by weight on the weight of the ore of "Corson Regular" lime. To this was added 7% water. The mixture was divided into two portions. To one portion was added 0.2% calcium chloride. To the other portion was added 0.2% calcium chloride and 0.5% blackstrap molasses. The two portions were subject to an atmosphere of 100% carbon dioxide for 2½ hours. The resulting briquettes were tumbled as in Example I. The results appear in Table IX.

Table IX

Material	Percent by Weight	Average Tumble Test
Liberian Ore Fines	100	
Corson Regular	5	
Calcium Chloride	0.2	56
Water	7	
Liberian Ore Fines	100	
Corson Regular	5	
Calcium Chloride	0.2	85
Blackstrap Molasses	0.5	
Water	7	

EXAMPLE X

Venz Lilo Ore was mixed with 5% Corson Regular lime and 9% water. To the mixture was added 0.031% Versene (tetra sodium salt of ethylene diamine tetra acetic acid) and 0.2% calcium chloride. Briquettes were formed, carbonated and tumbled as in Example I. The tumble test was 76. Repeating with 0.05% Versene gave a tumble test of 82.

Similar results were obtained with mixtures containing up to 1% Versene.

Comparison of the foregoing test results will show that soluble carbohydrates such as starches and sugars, either as crystalline materials or as syrups and other solubilizing agents for calcium and magnesium such as Versene are effective to markedly increase the rate of formation of hardened briquettes and to reduce the degree of attrition of briquettes from tumbling as shown by the screen residue tests.

The very significant increase in rate of formation is illustrated in the accompanying drawing showing comparative results of rate tests made by carbonating briquettes made of a mixture of 100 parts Venz Lilo ore, 0.2 part calcium chloride, and 5 parts Ohio superfine lime, with and without the addition of 0.5 part of molasses for varied periods of time and tumbling the resulting briquettes as in the case of Example 1.

While I have described certain preferred practices and products according to my invention, it will be understood that this invention may be otherwise practiced within the scope of the following claims.

I claim:

1. The method of producing lump ore from finely divided iron containing materials, comprising the steps of admixing the finely divided material with at least one of the group consisting of the oxides and hydroxides of alkaline earth metals and with a material capable of solubilizing alkaline earth metals selected from the group consisting of water soluble carbohydrates and the so-

dium salt of ethylene-diamine tetra acetic acid, forming the mixture into lumps and reacting the resulting lumps with carbon dioxide in the presence of moisture to form alkaline earth carbonates prior to charging in a metallurgical furnace.

2. The method of producing lump ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the group consisting of the oxides and hydroxides of alkaline earth metals and mixtures thereof, with a sugar containing material, forming the mixture into lumps, and reacting the resulting lumps with carbon dioxide in the presence of moisture to form alkaline earth carbonates prior to charging in a metallurgical furnace.

3. The method of producing lump ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the group consisting of the oxides and hydroxides of alkaline earth metals and a material capable of solubilizing alkaline earth metals selected from the group consisting of water soluble carbohydrates and the sodium salt of ethylene-diamine tetra acetic acid, forming the mixture into lumps and reacting the resulting mixture with carbonic acid gas in the presence of up to about 10% moisture and at least one soluble salt from the group consisting of the chlorides, sulfates and carbonates of alkali metals, alkaline earth metals and iron to form alkaline earth carbonates prior to charging in a metallurgical furnace.

4. The method of producing lump ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the oxides and hydroxides of calcium and a soluble carbohydrate in the presence of moisture, forming the resulting mixture into lumps and reacting the formed lumps with carbonic acid gas in the presence of up to about 10% moisture prior to charging in a metallurgical furnace to cause crystallization of calcium carbonates in the interstices of the formed lumps.

5. The method of producing lump iron ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the oxides and hydroxides of calcium and at least one sugar containing material, forming the mixture into lumps, and reacting the resulting mixture with carbon dioxide in the presence of up to about 10% moisture prior to charging in a metallurgical furnace whereby to form calcium carbonate in the formed lumps.

6. The method of producing lump iron ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the oxides and hydroxides of calcium together with at least one starch containing material and reacting the resulting mixture with carbon dioxide in the presence of up to about 10% moisture prior to charging in a metallurgical furnace whereby to form calcium carbonate in the formed lumps.

7. The method of producing lump iron ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the oxides and hydroxides of magnesium and calcium and reacting the resulting mixture prior to charging in a metallurgical furnace with carbonic acid gas to form magnesium and calcium carbonates in the presence of up to about 10% moisture, at least one soluble salt from the group consisting of the chlorides of the alkali metals, alkaline earth metals and iron and at least one solubilizing agent for magnesium and calcium selected from the group consisting of water soluble carbohydrates and the sodium salt of ethylene-diamene tetra acetic acid.

8. The method of producing lump iron ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the oxides and hydroxides of calcium and glucose in the presence of moisture, forming the resulting mixture into lumps and reacting the formed lumps prior to charging in a metallurgical furnace with carbonic acid gas in the presence of up to about 10% moisture to cause crystallization of calcium carbonate in the interstices of the formed lumps.

9. The method of producing lump iron ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the oxides and hydroxides of calcium and maltose in the presence of moisture, forming the resulting mixture into lumps and reacting the formed lumps prior to charging in a metallurgical furnace with carbonic acid gas in the presence of up to about 10% moisture to cause crystallization of calcium carbonate in the interstices of the formed lumps.

10. The method of producing lump iron ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the oxides and hydroxides of calcium and dextrose in the presence of moisture, forming the resulting mixture into lumps and reacting the formed lumps prior to charging in a metallurgical furnace with carbonic acid gas in the presence of up to about 10% moisture to cause crystallization of calcium carbonate in the interstices of the formed lumps.

11. The method of producing lump iron ore from finely divided iron-containing materials, comprising the steps of admixing the finely divided material with at least one of the oxides of hydroxides and calcium and fructose in the presence of moisture, forming the resulting mixture into lumps and reacting the formed lumps prior to charging in a metallurgical furnace with carbonic acid gas in the presence of up to about 10% moisture to cause crystallization of calcium carbonate in the interstices of the formed lumps.

12. The method of producing lump iron ore from finely divided iron-containing materials, comprising the steps of admixing the finely ground material with at least one of the group consisting of the alkaline earth metal oxides and hydroxides in an amount equivalent to about 2% to 8% of oxide based on the dry weight of the ore, and from about 0.025% to 2% by weight of a solubilizing agent for alkaline earth metals selected from the group consisting of water soluble carbohydrates and the sodium salt of ethylene-diamine tetra acetic acid, forming the resulting mixture into lumps in the presence of up to about 10% moisture, and reacting the formed lumps with carbon dioxide to convert at least a part of the admixed member of the group oxide and hydroxide to carbonate, prior to charging in a metallurgical furnace.

13. A lump ore product produced from finely divided iron-containing materials, comprising a formed matrix of said finely divided iron material bound together by alkaline earth metal carbonate formed in situ by the steps of admixing the iron material with a material selected from the group consisting of oxides and hydroxides of alkaline earth materials, a material selected from the group consisting of water soluble carbohydrates and the sodium salt of ethylene-diamine tetra acetic acid, and reacting the mixture with carbon dioxide in the presence of up to 10% moisture.

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CERTIFICATE OF CORRECTION

Patent No. 2,996,372 August 15, 1961

Louis George Imperato, Jr.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 30, for "of hydroxides and" read -- and hydroxides of --.

Signed and sealed this 6th day of February 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents