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⑦① Applicant: **KAISER ALUMINUM & CHEMICAL CORPORATION, 865 Kaiser Building 300 Lakeside Drive, Oakland California 94643 (US)**

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⑦② Inventor: **Cassens, Nicholas, 4082 Suffolk Way, Pleasanton California 94566 (US)**

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⑦④ Representative: **Oliver, Roy Edward et al, POLLAK, MERCER & TENCH Chancery House 53-64 Chancery Lane, London WC2A 1HJ (GB)**

⑥④ **Plastic chrome ore refractory compositions.**

⑥⑦ In order to provide plastic chrome ore refractory compositions which have a desirably low swelling or bloating tendency, without using asbestos or floc, compositions are introduced, which include hectorite, which is a naturally occurring or manufactured hydrous magnesium silicate material. The refractory compositions contain, by weight on a dry basis, 85 to 95% of size-graded chrome ore, 1 to 5% of alkali metal silicate binder, 0 to 5% of plasticizer (other than hectorite) and sufficient water to form a plastic mass, the amount of hectorite being 0.5 to 5%. The hectorite can constitute the sole plasticizer, but for cost reasons other plasticizers are also included, plastic clays being especially preferred.

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Plastic Chrome Ore Refractory Compositions

This invention relates to plastic chrome ore refractory compositions. The invention is concerned with refractory compositions comprising 85% to 95% size-graded chrome ore, 1% to 5% of alkali metal silicate binder, 0% to 5% of a plasticizer other than hectorite and sufficient water to form a plastic mass, all percentages being by weight and based on the total dry weight of the ingredients. The amount of alkali metal silicate binder stated is calculated as sodium silicate.

10 Plastic chrome ores are well-known in the refractories industry and are described, for example, in U.S. Patent Specifications 2,792,311, 2,965,505 and 3,297,458.

U.S. Patent Specification 3,297,458 discloses a solution to the problem that some plastic chrome ore
15 refractory compositions bloat or swell under conditions of rapid heating. Specifically, it discloses the addition of floc or asbestos in minor amounts to these compositions, in order to prevent such swelling or bloating.

Although the compositions described in U.S. Patent
20 Specification 3,297,458 have proved commercially successful, particularly when they include asbestos, there is some concern that asbestos may pose a health hazard and, accordingly, it is desirable to produce a non-bloating plastic chrome ore composition which does not require the use of
25 asbestos.

The present invention is directed to the solution of this problem.

The invention is based upon the discovery that any undesirable tendency to swell or bloat is minimized or even
30 eliminated if the refractory composition includes 0.5% to 5% of hectorite, the percentage amount being by weight and based upon the total dry weight of the ingredients of the composition.

The chrome ore used can be any of such materials,
35 either natural or synthetic, well-known in this art. Size-

graded chrome ore is used, in order to achieve good density upon placement of the refractory compositions, as will be well understood. For example, the chrome ore may all be less than 9.5 mm in diameter and size-graded so that roughly 5 one-third is greater than 2 mm in diameter, roughly one-third is less than 2 mm in diameter and greater than 0.15 mm in diameter and roughly one-third is less than 0.15 mm in diameter. This size grading means that all the chrome ore passes a 3/8 inch mesh screen, roughly one-third is retained 10 on a 9-mesh screen, one-third is retained on a 100-mesh screen and the remaining one-third passes a 100-mesh screen.

Hectorite is a hydrous silicate of magnesium and lithium, sometimes containing fluorine, and occurs naturally near Hector, California, United States of America. It has 15 also been produced synthetically and either form can be used in carrying out this invention. However, the natural material is preferred, particularly a refined grade of the natural material. Hectorite is a well-known material which has been used in many compositions, including refractory gun 20 mixes, for example as disclosed in U.S. Patent Specification 2,407,725. It has also been used as a coating on refractory material, for example chrome ore, as disclosed in U.S. Patent Specification 2,406,910.

The binder material may be any of the many well-known 25 varieties of sodium silicate. It is believed that it is the swelling action of the sodium silicate binder upon drying which leads to bloating of conventional plastic chrome compositions and that such bloating tendency is higher when a sodium silicate of relatively high silica content is used. 30 Accordingly, this invention is particularly useful with such high silica sodium silicates. The sodium silicate can be added either dry or in liquid form; the latter form has proved to be particularly convenient. However, in which-ever form (dry or liquid solution) the sodium silicate is 35 added, the percentage amounts given in the specification and

claims refer to the amount of dry material added. In other words, if a solution is added, the percent of sodium silicate added is the amount of that material in the solution (i.e., the amount obtained upon drying the solution). Other, 5 equivalent alkali metal silicates, for example lithium silicate, can be used.

While a plasticizer is not essential, it has been found to impart improved workability to the plastic chrome ore and the inclusion of a plasticizer is therefore preferred. 10 The plasticizer can be any of the many well-known materials of this type, for example, it can be an organic material, e.g. methyl cellulose. However, a clay, particularly a plastic kaolin type of clay, has proved particularly useful in making compositions according to this invention.

15 As used in this specification, the term "clay" means a hydrous aluminosilicate type of mineral, for example of the kaolinite type, which exhibits lubricity and plasticity when admixed with water. See, for example, the definition of "clay" in Ceramic Glossary (American Ceramic Society, 20 1963). The term "clay" is particularly to be distinguished from the hectorite used in compositions according to the present invention, which is a magnesium silicate mineral.

It is possible to omit entirely the plasticizer in the composition, relying on the hectorite, and perhaps 25 increasing its amount, to provide the workability desired in the composition. However, this approach will generally prove uneconomic, since there are many clay materials which are considerably cheaper than hectorite.

In making a composition according to this invention, 30 the sized chrome ore and other ingredients are mixed together, for example in a Muller mixer, and sufficient water is then added to form a plastic mass. The precise amount of water to be added depends upon the types and amounts and sizing of the materials used, including the 35 form in which the sodium silicate or other binder is added,

but will generally range from 1% to 5% by weight, based on the total weight of the composition.

The composition can also contain other ingredients, without departing from the scope of this invention. For example, it can contain a sequestering agent (for example, ethylene diamine tetra-acetic acid), which prevents premature reaction, and consequent setting of the mix, between the sodium silicate binder and any stray magnesia which may have got into the composition.

10 As used in the specification and claims, the expression "based on the total dry weight of the ingredients" means that the weight percentages given are based upon the amount of material which would be found in the composition after it had been dried; that is to say, after any water, whether
15 added to form the plastic mass, added as part of the alkali metal silicate binder solution or added with any sequestering agent solution, had been removed.

Example

A plastic chrome ore refractory composition according
20 to this invention was made from 88.3 parts of sized Transvaal chrome ore, 7.83 parts of RU grade sodium silicate (an aqueous solution of sodium silicate made by Philadelphia Quartz Co. having 13.8% Na_2O , 33.2% SiO_2 and a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.4:1), 2.62 parts of Hamilton II clay (a plastic
25 kaolin), 0.25 part of Versene (an ethylene diamine tetra-acetic acid sequestering agent) and 1 part of Baroid Macaloid, a refined hectorite ore. A 15 kg batch of this composition was mixed in a small Muller mixer, together with 2.2 parts of water (in addition to the water contained in the sodium
30 silicate solution). As will be apparent, the mixture contained on the dry basis 92.4% of chrome ore, 3.9% of sodium silicate, 2.7% of clay and slightly over 1% of hectorite.

The Transvaal chrome ore was sized so that all was less than 9.5 mm in diameter (i.e., all passed a 3/8 inch
35 mesh screen) and 28.1 parts were greater than 2 mm in

diameter (i.e., were retained on a 9-mesh screen), 28.1 parts were smaller than 2 mm and larger than 0.15 mm (i.e., retained on a 100-mesh screen), and 32.1 parts were smaller than 0.15 mm. The chrome ore over 2 mm in size had the following typical chemical analysis (ignited basis): 11.1% MgO, 0.4% CaO, 8.2% SiO₂, 14.5% Al₂O₃, 39.7% Cr₂O₃ and 26.1% Fe₂O₃; and that under 2 mm in size, a beneficiated ore, the following typical analysis: 44.1% Cr₂O₃, 28.7% Fe₂O₃, 15.1% Al₂O₃, 9.7% MgO, 0.2% CaO and 2.2% SiO₂. The Hamilton clay and the hectorite were both substantially all less than 44 microns in size (i.e., both all passed a 325-mesh screen) and the Versene was in the form of an aqueous solution.

This composition was tested for bloating by hand ramming it into a can 10.5 cm in diameter by 12 cm high using a 20 mm (3/4 in) diameter steel rod. The excess material was cut off with the edge of a trowel and the top surface smoothed. Four vent holes were made in the exposed surface with a 3 mm (1/8 in) diameter welding rod to a depth of 5 cm (2 in). After the material had dried for 48 hours at room temperature and had then been dried in an oven for 16 hours at 120°C (250°F), the height of the specimen above the rim of the can was measured and found to be 11.5 mm (0.46 in). The material was also stored in plastic bags for a total of 16 weeks, after which time it still remained plastic.

This composition can be compared with another composition made in the same way except that, in place of the hectorite, 1 part of Volclay, a plastic bentonite clay, was used, and 1.5 parts of water were used. Although this comparison composition remained plastic after storage for 12 weeks, in the bloat test it showed an increased height of 23.5 mm (0.92 in), an unacceptably high amount.

In addition to the two foregoing compositions, 35 additional similar compositions were made using the following

additives in place of the hectorite or Volclay bentonite: alumina dust collector fines, perlite, expanded vermiculite, both chopped and ball milled aluminosilicate glass fibres, cattle hair, volatilized silica, kyanite, rice hull ash, 5 mica, wollastonite, pyrophyllite, fibrous talc, diatomaceous earth and waste material from rug manufacture. Many of these comparison compositions failed to maintain their plasticity during storage, becoming set in a matter of a week or two. Others, although they did not set up 10 prematurely, showed bloating of from 20 to 44 mm (0.78 to 1.73 in), all unacceptably high.

For comparison purposes, a similar composition made with 1 part of asbestos, as disclosed in U.S. Patent Specification 3,297,458, showed a bloat of 11.5 mm (0.45 in), 15 with good storage for 16 weeks.

Each of the bloat heights reported is the average of two separate tests on the same composition.

Although the reason why hectorite, and the previously known asbestos and floc, prevent excessive bloating of these 20 plastic chrome ore compositions is not known with certainty (and applicant does not wish to be bound to any theory), the results of a very large number of tests indicate that as the rammed bulk density of the compositions increases, their tendency to bloat also increases. From these results, the 25 following empirical equation relating bloat height (in inches) to rammed density (in pounds per cubic foot, pcf) has been developed:

$$(1) \text{ Bloat} = -13.57 + 0.067 \times \text{Density};$$

or, in metric units,

$$30 \quad (2) \text{ Bloat (mm)} = -344.7 + 106.1 \times \text{Density (g/cc)}.$$

From many years experience with these plastic chrome compositions, it has been determined that a bloat (in the standard test described) of 16 mm (0.625 in) is the maximum 35 acceptable if the composition is to perform satisfactorily

in service. From the above empirical relationship, it can be determined that compositions with an acceptably low bloat will have a rammed bulk density of less than about 3.4 g/cc (212 pcf). From these many tests, it appears
5 that only hectorite (or asbestos or floc) additions yield compositions with an adequately low rammed bulk density to have adequately low bloat, combined with good storage life. In other words, it appears that the inclusion of these materials in the composition leads to a relatively
10 low density, an open structure which permits any expansion which occurs upon heating of the sodium silicate or other silicate binder to be absorbed within voids in the structure, rather than expanding the structure of the refractory itself.

15 In the specification and claims, percentages and parts are by weight unless otherwise indicated. Mesh sizes referred to herein are Tyler standard screen sizes which are defined in Chemical Engineers' Handbook, John H. Perry, Editor-in-Chief, Third Edition, 1950, published by
20 McGraw Hill Book Company, at page 963. For example, a 100 mesh screen opening corresponds to 147 microns. Analyses of mineral components are reported in the usual manner, expressed as simple oxides, e.g. MgO and Cr_2O_3 , although the components may actually be present in various
25 combinations, e.g. as a magnesium chromite.

Claims:

1. A plastic chrome ore refractory composition, comprising 85% to 95% of size-graded chrome ore, 1% to 5% of
5 alkali metal silicate binder, 0% to 5% of plasticizer other than hectorite and sufficient water to form a plastic mass, characterised in
that the composition also comprises 0.5% to 5% of hectorite, all percentages being by weight and based on the total dry
10 weight of the ingredients.
2. A refractory composition according to claim 1, wherein the hectorite is a natural hectorite.
3. A refractory composition according to claim 2, wherein the natural hectorite is a refined hectorite.
- 15 4. A refractory composition according to claim 1, 2 or 3, wherein 0.1% to 5% of plasticizer is present.
5. A refractory composition according to claim 4, wherein from 1% to 5% of clay is present as plasticizer.
6. A refractory composition according to claim 5, wherein
20 the clay is of the plastic kaolin type.
7. A refractory composition according to any preceding claim, wherein the sodium silicate binder is added as a liquid solution.
8. A refractory composition according to any preceding
25 claim, wherein the chrome ore is of the Transvaal type.



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
-	GB - A - 1 002 486 (LAVING) --	1, 4, 5, 6, 7	C 04 B 35-42 35-66
-	GB - A - 1 069 968 (HARBISON-WALKER) --	4, 5, 7	
-	FR - A - 1 321 817 (RUSSELL et al) * page 1, right column, line 19 *	8	
DA	US - A - 2 406 910 (SCHOENLAUB) * column 3, lines 10 to 14 *	1, 2	TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 04 B 35-00 C 04 B 35-12 C 04 B 35-42 C 04 B 35-66
A	DE - C - 677 322 (Dr. V.M. GOLDSCHMIDT) ----		
X The present search report has been drawn up for all claims			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons &: member of the same patent family, corresponding document
Place of search	Date of completion of the search	Examiner	
Berlin	08-11-1978	HÖRNER	