

# UNITED STATES PATENT OFFICE.

JAMES C. GRAVES, OF MIDLAND, MICHIGAN, AND JOHN P. SIMONS, OF CLEVELAND, OHIO, ASSIGNORS TO THE DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF MICHIGAN.

## METHOD OF MAKING HALOIDS.

964,156.

Specification of Letters Patent.

Patented July 12, 1910.

No Drawing.

Application filed August 6, 1909. Serial No. 511,511.

To all whom it may concern:

Be it known that we, JAMES C. GRAVES and JOHN P. SIMONS, both citizens of the United States, residents of Midland, county of Midland, and State of Michigan, and of Cleveland, county of Cuyahoga, and State of Ohio, have jointly invented a new and useful Improvement in Methods of Making Haloids, of which the following is a specification, the principle of the invention being herein explained and the best mode in which we have contemplated applying that principle, so as to distinguish it from other inventions.

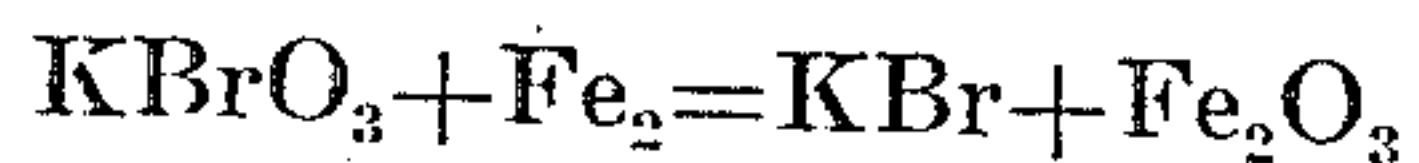
The present invention, relating, as indicated, to the making of haloids, has more particular regard to the manufacture of such compounds by reduction of the corresponding tri-oxygen salt. In other words, such process relates to the making of a chlorid, bromid or iodid from a chlorate, bromate, or iodate, specifically a bromate, chlorate, or iodate of an alkali or of an alkaline earth. Said invention, then consists of the means and steps hereinafter fully described and particularly pointed out in the claims.

When bromin combines with potassium hydrate or carbonate some potassium bromate is formed and at the same time a little hypobromite. This hypobromite, however, readily goes over to the bromate partially in the cold and completely on heating. In order to recover pure potassium bromid from the resulting mixture of potassium bromid and bromate the prevailing process heretofore has been to heat such mixture to a red heat. This of course involves the preliminary evaporation of the solution of bromid and bromate to dryness and then subsequently raising the same to such red heat, as a result of which not only is a considerable mechanical loss incurred incidentally to handling the material but also more or less loss through volatilization in the heating operation.

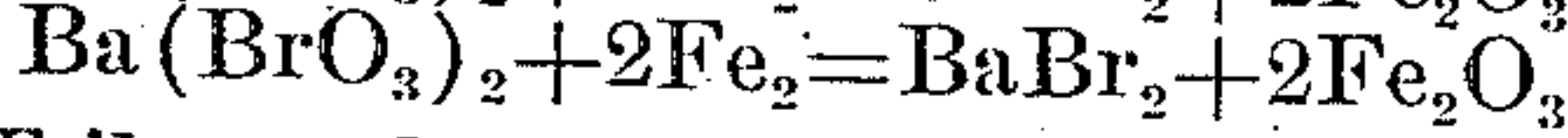
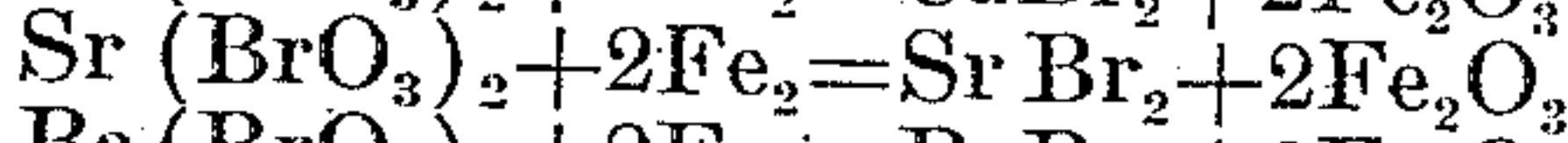
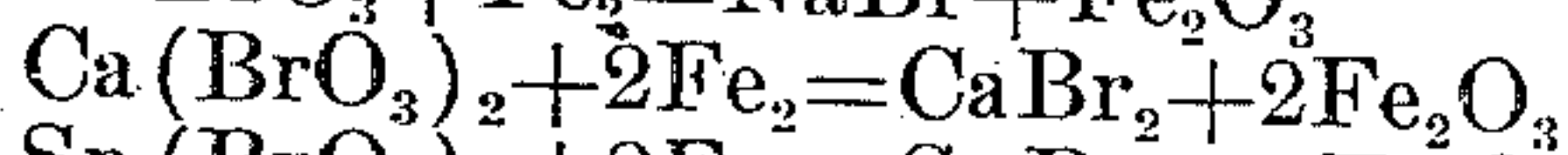
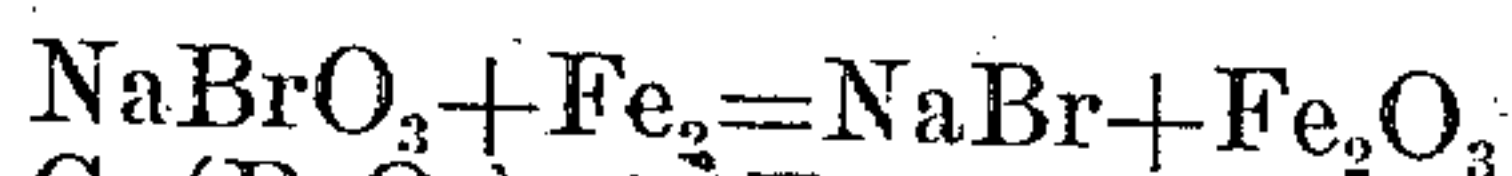
The object of the present invention is to substitute for such evaporating to dryness and subsequent heating, a wet process that will produce a precipitate susceptible of being easily washed free from accompanying bromid. We are aware that potassium bromid has been prepared by a wet process by the action of bromid of iron on either potassium hydrate or potassium carbonate;

but this method likewise is objectionable, having the great disadvantage that a voluminous iron precipitate is formed that is hard to wash, so that in practice more or less bromid always remains with the iron hydrate and is lost.

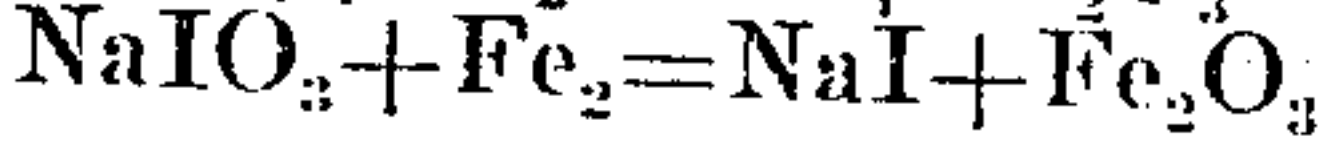
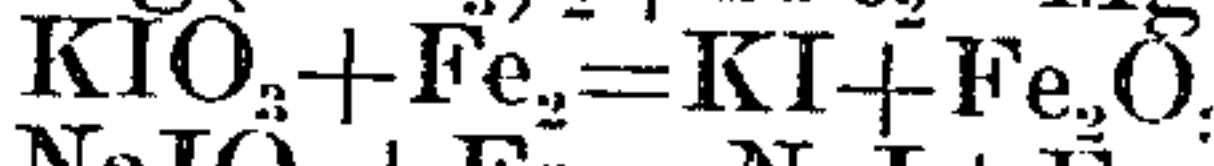
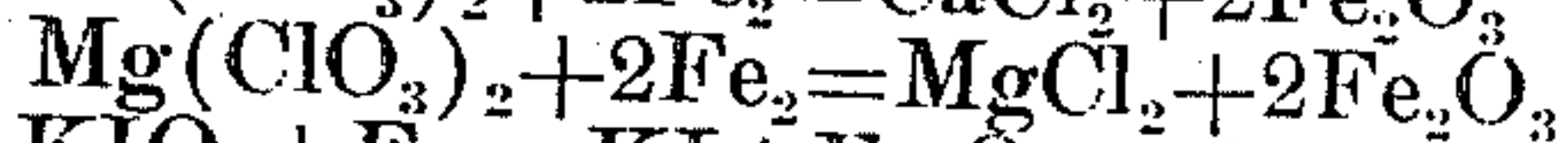
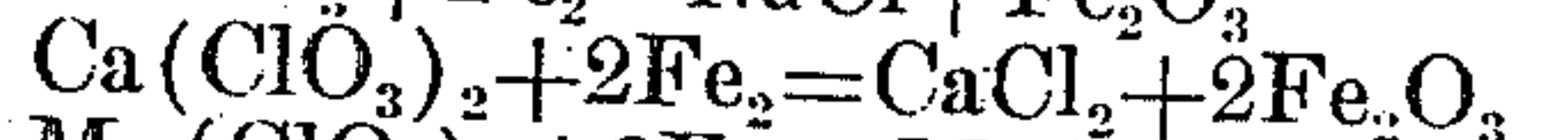
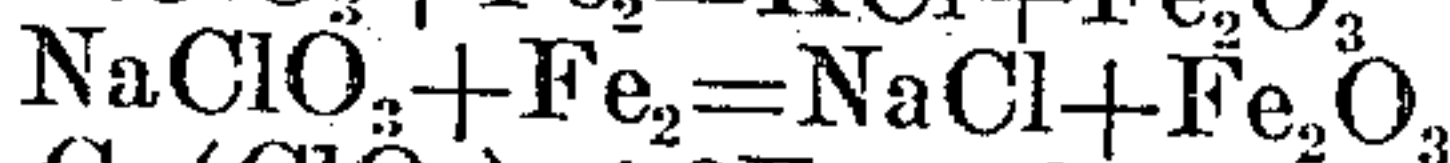
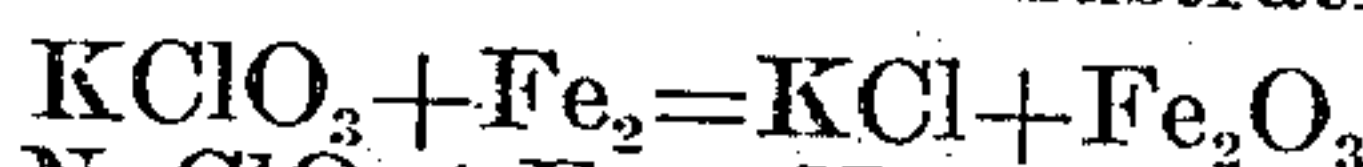
In the reduction of bromate of potash by our improved process the mixture of potassium bromid, bromate and hypobromite in solution is charged into a tank, together with a quantity of finely divided iron. This tank contains an agitator that revolves near the bottom of the tank so that the iron is mixed with the solution and is prevented from subsiding and forming a compact mass on the bottom. The following reaction thereupon takes place between the bromate and the iron:—



This reaction is accompanied by the liberation of considerable heat, which decomposes any remaining hypobromites, converting them into bromid and bromate. The agitation of the iron and liquor is continued until all the bromate is reduced, external heat being applied if found necessary. The solid material remaining in the tank is largely a dense iron oxid that is easily washed free from the accompanying liquor by filtration, and washing methods, well known to persons versed in chemical manufacture. This method is applicable in the same way to the reduction of other bromates such as those of sodium, calcium, strontium and barium, the reactions being as follows:—



While we have described the application of our invention to the reduction of a bromate to a bromid, it is equally applicable to the similar reduction of other tri-oxygen salts, chlorates and iodates. The following reactions will serve as illustrations:—



An important application of the first and



second reactions of the series given last above is to be found in the electrolytic alkali industry in the elimination of chlorates of potassium or sodium from the brine fed to the cells. This chlorate enters as a necessary evil in this industry due to the secondary reactions which take place between the principal products of electrolysis, *i. e.* caustic and chlorin. In practice, only a part of the chlorid fed to a cell is converted into caustic and chlorin, and when the cathode effluent, which contains the caustic produced by the electrolysis together with the undecomposed chlorid and some chlorate, both in solution, is concentrated by boiling, such chlorid separates out. This separated salt carries a part of the chlorate present in the cell effluent, and when it is re-dissolved and added to fresh chlorid to make fresh brine for the cell, the contaminating chlorate is also dissolved. If such contaminated solution be then fed to the cell, excessive electrode consumption and lowered economy will result. We have found that if such contaminated solution be treated with finely divided iron as hereinbefore described, with the application of heat, if necessary, the chlorate will be reduced to chlorid with precipitation of the oxid of iron, and a substantially pure solution of the haloid secured. It will of course be understood that other suitable means for bringing the iron and the bromate, or other salt, together may be employed instead of the one hereinbefore described, but such described means have been found convenient and satisfactory in practice. The iron which we use is preferably cast iron and is best employed, as has been stated, in more or less finely divided form, machine borings serving admirably for this purpose. The application of heat is not necessary but hastens the reaction, a temperature of 90 degrees centigrade being recommended. The time required to reduce 600 lbs. of the bromate will under favorable operative conditions be between 8 and 12 hours.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the process herein disclosed, provided the steps stated by any one of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. The method of making a haloid from the corresponding tri-oxygen salt, which consists in treating said salt in a water solution with metallic iron.

2. The method of reducing the tri-oxygen salt of a halogen to the corresponding haloid, which consists in treating the same in a water solution with finely divided cast iron.

3. The method of making a chlorid from the corresponding chlorate, which consists in treating said chlorate in a water solution with metallic iron.

4. The method of reducing an alkaline chlorate to the corresponding chlorid, which consists in treating the said chlorate in a water solution with finely divided cast iron.

5. The method of making potassium chlorid from potassium chlorate, which consists in treating the said chlorate in a water solution with metallic iron.

6. In the electrolytic production of alkalis from their haloid compounds, the steps which consist in recovering the haloid from the cell effluent, and then eliminating the tri-oxygen salt of the halogen from such haloid, substantially as described.

7. In the electrolytic production of alkalis from their haloid compounds, the steps which consist in recovering the haloid from the cell effluent, and then eliminating the tri-oxygen salt of the halogen from such haloid by treating the same in a water solution with metallic iron.

8. In the electrolytic production of alkalis from their haloid compounds, the steps which consist in recovering the haloid from the cell effluent, and then eliminating the tri-oxygen salt of the halogen from such haloid by treating the same in a water solution with finely divided cast iron.

9. In the electrolytic production of alkalis from their chlorids, the steps which consist in recovering the chlorid from the cell effluent, and then eliminating the chlorate from such chlorid, by treating the same with metallic iron.

10. The method of making a haloid from the corresponding tri oxygen salt, which consists in treating said salt in a water solution with metallic iron, whereby the latter is precipitated as an oxid, and then washing such oxid.

11. The method of making a haloid from the corresponding tri oxygen salt, which consists in treating said salt in a water solution with finely divided cast iron, whereby the latter is precipitated as a dense oxid, and then washing such oxid.

Signed by JAMES C. GRAVES, this 8th day of July, 1909.

JAMES C. GRAVES.

Attested by—

HARBEN H. DOW,  
RUPERT E. PARIS.

Signed by JOHN P. SIMONS, this 3 day of August, 1909.

JOHN P. SIMONS.

Attested by—

D. T. DAVIES,  
H. F. HADDE.