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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process of recovering Cassiterite and other Tin Oxides from Ores or other Materials containing same

We, RENISON LIMITED (incorporated in Victoria-Australia), of 65 William Street, Melbourne, Victoria, Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for recovering tin oxides and especially the mineral cassiterite (SnO_2) from other constituents of the ores or other source materials in which they occur, and is concerned with obtaining maximum recovery of the cassiterite from certain ores in which it is very finely disseminated, such as ores of the Renison district of Tasmania, in the Commonwealth of Australia.

In Renison district ores particularly, the cassiterite has a very fine grain structure, much of it occurring in the minus 325 mesh range (Tyler series) and the overall tin content being 0.1% by weight or higher depending from which part of the district the ore comes. The ultra fine grains are widely dispersed throughout and intimately associated with the gangue minerals, which are chiefly sulfides and to a lesser extent carbonates, silica, silicates and borosilicates. Among the sulfides, pyrrhotite predominates. There are relatively minor amounts of arsenopyrite and chalcopyrite and other sulfides.

Conventional processes for treating ore of this type rely entirely on gravity concentration techniques for recovering the cassiterite down to approximately the limits defined by normal vanner concentration methods. Particles smaller than 15 microns are normally lost to the gravity tailings under commercial conditions of operation.

In accordance with the present process, a major proportion of the fine particles of cassiterite are recovered by froth flotation utilizing a combination of flotation reagents not heretofore visualized as useful for the present purpose.

[Price 4s. 6d.]

The reagents employed for floating the ultra small particles of cassiterite, and which can also be employed for floating larger particles where there is any economic advantage in doing so as compared with customary gravity concentration techniques such as jigging, tabling, and vanning, are a mineral acid and a petroleum sulfonate.

It is customary to treat Renison district ores by crushing and grinding for sulfide flotation; subjecting the crushed and ground ore to a froth flotation step, utilizing a collecting reagent (usually a xanthate) and a frother to separate the sulfide gangue minerals as a froth concentrate; classifying the flotation tailings to product several size-fractions for gravity separation of the cassiterite mineral; and applying to each fraction an appropriate gravity concentration technique for recovering as much as possible of the cassiterite mineral contained therein.

This same procedure may be utilized in advance of the cassiterite flotation step of the process of this invention whenever considered desirable or any part or all of such procedure can be dispensed with if considered desirable for any given application of the invention to a particular ore. In any event, the feed to the cassiterite flotation, whether it be gravity concentration tailings, sulfide flotation tailings, crushed and ground ore (if sulfide minerals are not significantly present), or other materials, such as flue dusts, which may contain tin oxides, is most desirably first washed free of colloidal slime materials, as by means of a conventional cyclone washing circuit in which a conditioning reagent, such as caustic soda, sodium silicate, or soda ash, is preferably utilized, and is then conditioned for the subsequent cassiterite flotation.

The cassiterite flotation in the process of the present invention is carried out under acid conditions.

The process according to the present invention for recovering tin oxide minerals and particularly tin oxide minerals having a very

fine grain structure such as cassiterite from tin oxide ores or other source materials containing tin oxide minerals in association with gangue minerals comprises the steps of removing colloidal slimes from the said material, subjecting the resulting decolloidized material to a froth flotation procedure under mineral acid conditions in the presence of petroleum sulfonate as a collector reagent for the tin oxide minerals and recovering the tin oxide minerals as a froth concentrate of the flotation step.

It is preferred to first condition with the mineral acid and then with the petroleum sulfonate collector reagent; whereupon the conditioned pulp is subjected to flotation to produce a tin rougher froth concentrate, which is usually passed through multiple cleaning stages to produce a final tin concentrate. This final concentrate, though sometimes lean by ordinary standards (being a minimum of about 4% Sn), is adapted to modern tin smelting practice.

The ores or other source materials may if necessary be first of all crushed or ground to yield a finely divided material suitable for flotation.

The invention will now be described with reference to the accompanying drawing which is a flow diagram of the overall process, showing the preferred way of treating an ore such as for example an ore occurring in a Renison district, the flow sheet indicating some optional variations that may be applied when found suitable for a particular ore.

As previously indicated and as shown in the flowsheet, the raw ore as mined is crushed and ground to preferably pass a Tyler series 48 mesh for further processing.

The present process was developed especially for the previously described, fine grained, cassiterite ores of the Renison district of Tasmania, but is applicable to other ores and materials containing tin oxides, for example Bolivian ores.

Crushing and grinding is accomplished in the usual manner and with the usual equipment to produce preferably a minus 48 mesh material as feed to a sulfide flotation step if the ore contains sulfide minerals, as both Renison and the customary Bolivian ores do. Customary reagents are used to yield a froth rich in the sulfide minerals, which is normally sent to waste.

The tailing from this sulfide flotation is preferably used as feed to gravity concentration for the recovery of particles of the tin mineral. Gravity concentration is accomplished in the usual manner by use of jigs, tables and vanners, preferably with accompanying desliming stages using cyclones or other known means to produce the usual tin concentrate.

The gravity tailing containing cassiterite, middling, and gangue particles (normally in the 10—25 micron size range) along with remaining colloidal slimes, is normally re-

garded as waste. In accordance with the invention, however, this tailing is processed for the recovery of the cassiterite and middling particles (most desirably after first removing the colloidal slimes) by floating the tin oxides from the associated gangue minerals.

A conventional cyclone washing circuit is preferably utilized for colloidal desliming, with or without additional gravity separation stages, depending upon the circumstances, and preferably employing a dispersing agent. Dispersing agents known to be useful for the purpose are alkali metal hydroxides, carbonates, and silicates, and combinations of one or more of these. The separated colloids are sent to waste, while the fine sands are utilized as flotation feed.

In accordance with the invention, this flotation feed is subjected to flotation in the presence of a mineral acid and a petroleum sulfonate. This is most desirably accomplished by first subjecting the flotation feed to conditioning with the mineral acid and with the petroleum sulfonate. Normally the acid treatment is effected first, although the order may be reversed or both conditioning operations be effected simultaneously. The petroleum sulfonate, aided by the mineral acid, serves as a collector reagent.

The acid is usually sulfuric, because of its low cost and availability. The quantity of acid may be controlled to bring the pH of the pulp undergoing conditioning within the range of substantially 1.0 to 3.5, but preferably to within the range of substantially 2.0—3.0. Lower pH is unnecessary and usually uneconomic. Higher pH progressively reduces the effectiveness of the process. Acid conditioning is usually completely accomplished in one minute. Various factors will determine the pH preferable for any given material. Simple practical testing in laboratory flotation equipment, as is common in the art, will indicate the pH preferable for any given use of the process of this invention.

For the conditioning step with the petroleum sulfonate collector reagent, which may be the proprietary product Flotation Reagent 801 as produced and sold by American Cyanamid Company, a quantity of the reagent (usually in the range of 0.5 to 2.0 pounds per ton of the ore or other material) is employed, depending upon the extent to which slimes have been successfully eliminated and other factors capable of practical test evaluation by those skilled in the art.

The conditioned pulp is then subjected to froth flotation in any of the standard makes of flotation machines, utilizing as many cleaner stages as may be found appropriate for any given ore or other material. Depending upon conditions, it may be necessary to stage add further acid and collector reagent, as indicated in the flowsheet, and to subject the pulp to an appropriate flotation time in order to

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achieve and maintain the highest possible recovery from rougher, scavenger and cleaner flotation procedures.

5 Several examples show the results of laboratory tests on vanner tailings derived from a cassiterite ore from the Renison district of Tasmania, Australia, which had been previously subjected to flotation for the removal of sulfide gangue materials. Generally similar
10 flotation test procedures were employed for all tests. The only test variable was whether or not a dispersing agent was utilized in the

desliming operation, and, if so, the kind. Procedure for all tests was as follows:

Referring to the following flotation conditions and ensuing examples the term "rougher" indicates "a primary flotation", "conditioner" indicates "a vessel for holding the material until reaction is completed", "scavenger flotation" means "flotation of the primary tailings", "cleaner flotation" means
15 "a refloatation step performed upon the concentrate".
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Flotation Conditions	Time	Reagents
Rougher Conditioner No. 1	1 min.	2.5 lbs/ton H_2SO_4
Rougher Conditioner No. 2	1 min.	0.5 lbs/ton R—801
Rougher Flotation	3 min.	
Scavenger Conditioner	1 min.	2.5 lbs/ton H_2SO_4 0.2 lbs/ton R—801
Scavenger Flotation	2 min.	
Cleaner Conditioner	1 min.	2.5 lbs/ton H_2SO_4
Cleaner Flotation	2 min.	

Percent weight solids in rougher flotation: 25%

Testing conducted in 1000 gram laboratory AGITAIR Flotation Machine. The pH in the rougher and scavenger flotation steps varied from 2.4 to 3.2, and in the cleaners, from 2.3 to 2.5. Only the rougher flotation concentrate was cleaned, and in only one stage.

EXAMPLE 1

No dispersant used in desliming.

Product	Sn %	Product Wt. %	Sn Distribution %	Wt. %*	*Sn Distribution %
Vanner tail	1.057	100.00	100.0	100.0	100.0
Discard slimes	1.222	48.16	55.7		
Sn Flotation feed	0.904	51.84	44.3	100.0	100.0
Sn scavenger tail	0.289	36.97	10.1	71.32	22.8
Sn scavenger concentrate	1.928	5.17	9.4	9.97	21.2
Sn rougher concentrate	2.703	9.70	24.8	18.71	56.0
Sn cleaner concentrate	4.193	3.61	14.3	6.96	3.22 32.2
Sn cleaner tailing	1.819	6.09	10.5	11.75	32.8 23.7
Combined rougher Sn concentrate & scavenger concentrate	2.434	14.87	34.2	28.68	77.7 77.2

* Based on feed to tin flotation

EXAMPLE II

NaOH at 10 lbs/ton Used in Desliming

Product	Sn %	Product Wt. %	Sn Distribution %	Wt. %*	Sn Distribution %*
Vanner tail	1.051	100.00	100.0	100.00	100.0
Discard slimes	1.220	48.32	56.1		
Sn flotation feed	0.894	51.68	43.9	100.00	100.0
Sn scavenger tail	0.193	33.31	6.1	64.46	13.9
Sn scavenger concentrate	0.867	4.79	3.9	9.27	8.9
Sn rougher concentrate	2.624	13.58	33.9	26.27	77.2
Sn cleaner concentrate	4.627	5.77	25.4	11.16	57.8
Sn cleaner tailing	1.144	7.81	8.5	15.11	19.4
Combined rougher Sn concentrate and scavenger concentrate	2.165	18.37	37.8	35.54	86.1

* Based on feed to tin flotation.

EXAMPLE III

Na₂SiO₃ at 10 lbs/ton Used in Desliming

Product	Sn %	Product Wt. %	Sn Distribution %	Wt. %*	Sn Distribution %*
Vanner tail	1.062	100.00	100.0	100.00	100.0
Discard slimes	1.217	48.81	55.9		
Sn flotation feed	0.914	51.19	44.1	100.00	100.0
Sn scavenger tail	0.177	33.03	5.5	64.53	12.5
Sn scavenger concentrate	0.869	4.79	3.9	9.36	8.8
Sn rougher concentrate	2.752	13.37	34.7	26.11	78.7
Sn cleaner concentrate	4.298	7.01	28.4	13.69	64.4
Sn cleaner tailing	1.048	6.36	6.3	12.42	14.3
Combined rougher Sn concentrate and scavenger concentrate	2.256	18.16	38.6	35.47	87.5

* Based on feed to tin flotation

5 The foregoing results show that an additional recovery of tin can be realized from a fraction of tin contained in the ore that formerly was lost in the slime and the fine sand fraction of the final tailings. The tin was observed to be both free and associated with other minerals in the above concentrate, which, although low grade by usual standards,

is amenable to smelting by modern techniques. 10
Other tests were made on samples of the sulfide flotation tailing directly, without the prior application of gravity separation techniques as in the foregoing examples, but preceded by the desliming procedures previously 15
described. The following is typical of these tests:

Flotation Conditions	Time	pH	Reagents
Rougher Conditioner No. 1	1 min.	2.0	10 lbs/ton H ₂ SO ₄
Rougher Conditioner No. 2	1/2 min.	2.0	2 lbs/ton R-801
Rougher Flotation	2 min.		
Cleaner No. 1 Conditioner	1 min.	2.1	5 lbs/ton H ₂ SO ₄
Cleaner No. 1 Flotation	2 min.		
Cleaner No. 2 Conditioner	1 min.	1.9	5 lbs/ton H ₂ SO ₄
Cleaner No. 2 Flotation	2 min.		

Percent weight solids in rougher flotation: 15%

Testing conducted in a 1000 gram laboratory AGITAIR Flotation Machine.

EXAMPLE IV

Product	Wt. %	Sn %	Sn Distribution %
Sulphide flotation tail	100.0	7.65	100.0
Sn rougher tail	62.1	0.533	4.3
Sn rougher concentrate	37.9	19.3	95.7
No. 1 Sn cleaner tailing	20.4	3.65	9.7
No. 1 Sn cleaner concentrate	17.5	37.6	86.0
No. 2 Sn cleaner tailing	2.9	6.40	2.5
No. 2 Sn cleaner concentrate	14.6	43.9	83.5

WHAT WE CLAIM IS:—

1. A process for recovering tin oxide minerals and particularly tin oxide minerals having a very fine grain structure such as cassiterite from tin oxide ores or other source materials containing such tin oxide minerals in association with gangue minerals comprising the steps of removing colloidal slimes from the said material, subjecting the resulting decolloidized material to a froth flotation procedure under mineral acid conditions in the presence of petroleum sulfonate as a collector reagent for the tin oxide minerals and recovering the tin oxide minerals as a froth concentrate of the flotation step.

2. The process claimed in Claim 1, wherein the colloidal slimes are removed from the finely divided material by passing such material through a cyclone washing circuit.

3. The process claimed in Claim 2, wherein at least one dispersing agent selected from alkali metal hydroxides, carbonates, and silicates is introduced into the cyclone washing circuit.

4. The process claimed in any one of the preceding claims, wherein the finely divided material contains sulfide minerals as gangue constituents, and such sulfide minerals are removed from the finely divided material by a froth flotation step in the presence of a collector for sulfide minerals prior to the removal of colloidal slimes therefrom.

5. The process claimed in any one of the preceding claims, wherein coarser particles of tin oxide minerals are removed from the more finely divided material prior to removal of colloidal slimes therefrom.

6. A process as claimed in any of the preceding claims, wherein the tin oxide is cassiterite having a very fine grain structure occurring for example in the Renison district of Tasmania.

7. The process claimed in Claim 6, wherein the colloidal slimes are removed from the ore after crushing and grinding the latter by passing such ore through a cyclone washing circuit.

8. The process claimed in Claim 7, wherein at least one dispersing agent selected from alkali metal hydroxides, carbonate, and silicates is introduced into the cyclone washing circuit.

9. A process for recovering tin oxide minerals from tin oxide ores or other source materials containing same, substantially as hereinbefore described with reference to the accompanying flowsheet.

For the Applicants,
F. J. CLEVELAND & COMPANY,
Chartered Patent Agents,
Lincoln's Inn Chambers,
40/43 Chancery Lane,
London, W.C.2

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For the Applicants,
F. J. CLEVELAND & COMPANY,
Chartered Patent Agents,
Lincoln's Inn Chambers,
40/43 Chancery Lane,
London, W.C.2

