

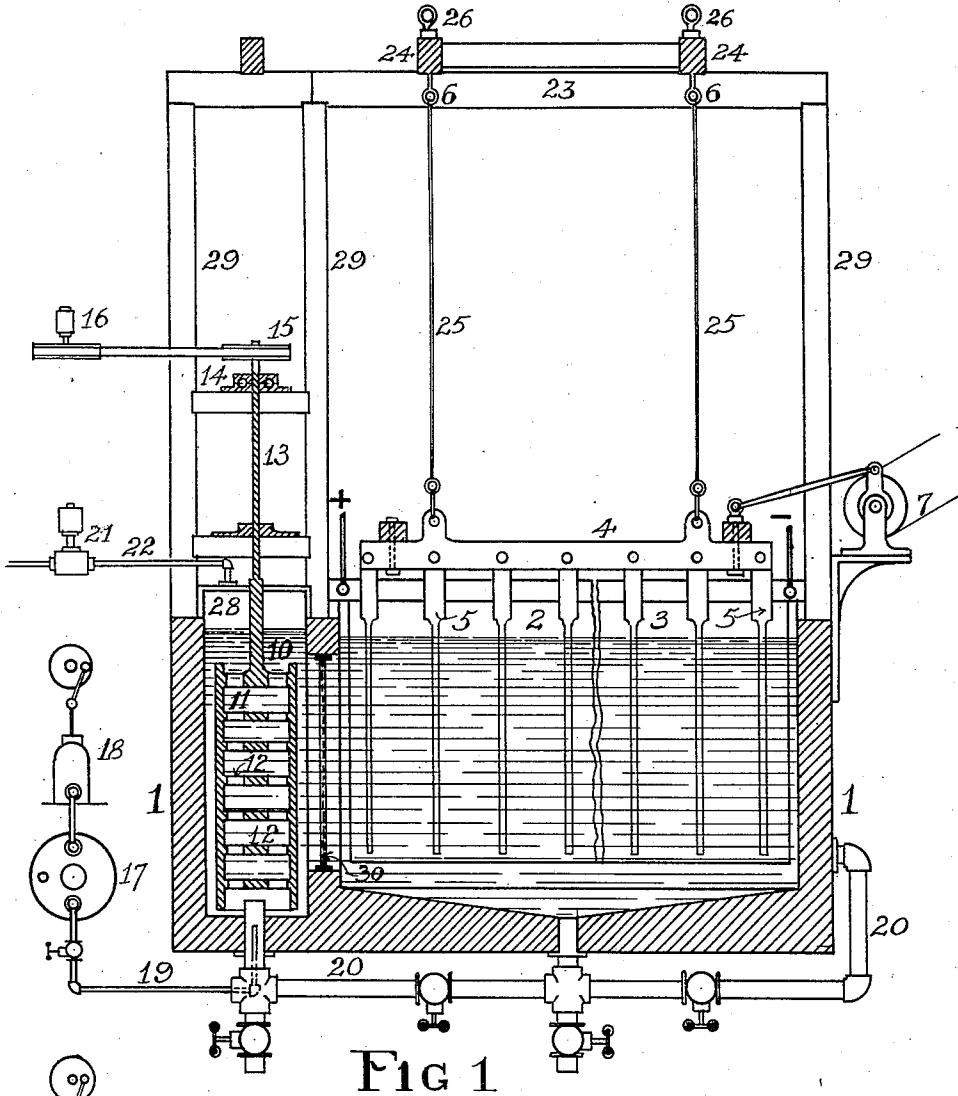
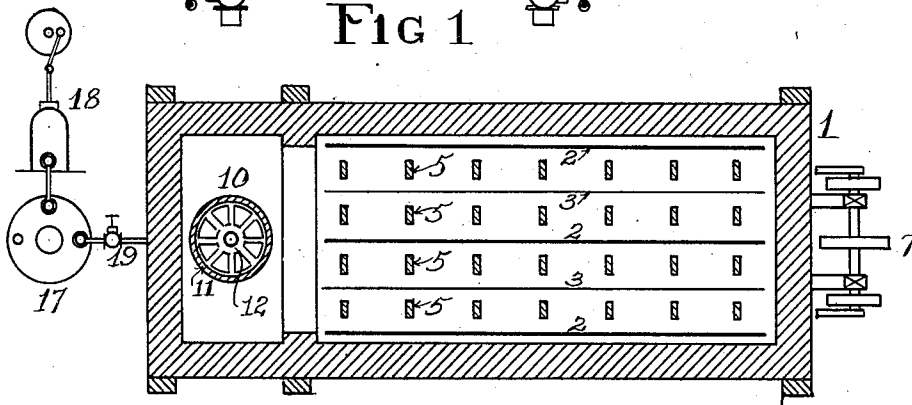
W. E. GREENAWALT.
ELECTROLYTIC PROCESS.

APPLICATION FILED FEB. 24, 1914. RENEWED FEB. 26, 1918.

1,279,860.

Patented Sept. 24, 1918.

2 SHEETS—SHEET 1.



WITNESSES

Jno. J. Hyer
Fred L. Scott

Fig 2

INVENTOR

William E. Greenawalt

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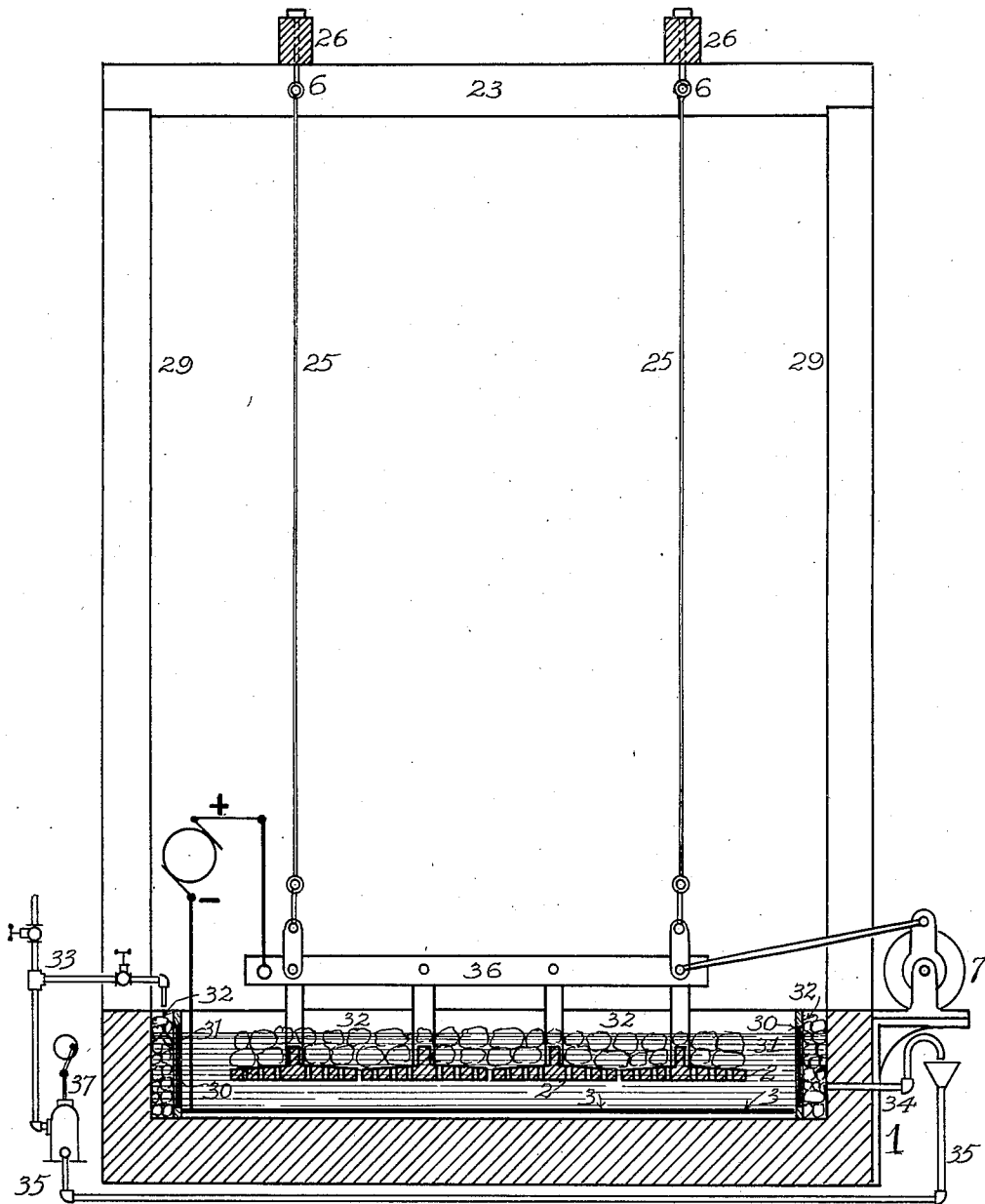


FIG 3

WITNESSES

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UNITED STATES PATENT OFFICE.

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ELECTROLYTIC PROCESS.

1,279,860.

Specification of Letters Patent. Patented Sept. 24, 1918.

Application filed February 24, 1914, Serial No. 820,496. Renewed February 26, 1918. Serial No. 219,840.

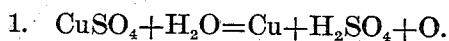
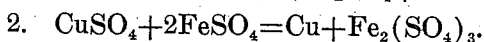
To all whom it may concern:

Be it known that I, WILLIAM E. GREENAWALT, a citizen of the United States, residing in the city and county of Denver and State of Colorado, have invented certain new and useful Improvements in Electrolytic Processes, of which the following is a specification.

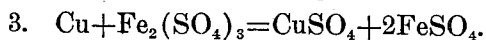
The invention relates to improvements in electrolytic processes, and has for its more immediate object the maintaining of the variable valent elements in an impure electrolyte at their lowest valency, and thus, to a large extent, increasing the cathode efficiency. The process will be described more particularly to the electrolysis of impure copper sulfate solutions, although it is not intended to limit it to this use alone.

In the electrolysis of impure copper sulfate solutions, as for example those obtained in leaching copper ores, there is always present iron sulfate, which injuriously affects the operation. Ferrous sulfate in the electrolyte is not particularly harmful, but the ferric sulfate is highly detrimental.

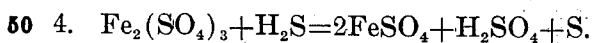
If a solution of copper sulfate, containing ferrous sulfate, is electrolyzed, copper is deposited at the cathode while sulfuric acid and ferric sulfate are produced at the anode, as represented by the following equations:



The ferric sulfate, finding its way back to the cathode, combines with the deposited copper and is again reduced to the ferrous condition, thus representing a loss of efficiency, as represented by equation:



If, however, the ferric sulfate can be reduced at the expense of a comparatively cheap reducing agent, such as hydrogen sulfid, then acid is regenerated, and the iron in the electrolyte loses its ability to combine with the deposited copper, as shown by the equation:

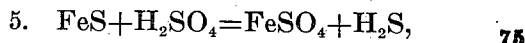


So that for every molecule of iron that is reduced from the ferric to the ferrous condition one molecule of acid is regenerated, and an atom of sulfur liberated. The acid is beneficial in the electrolyte, and on leaving

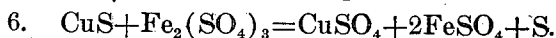
the electrolyzer, is further available for the extraction of copper from the ore.

The reduction of the ferric sulfate with hydrogen sulfid or its equivalent may be accomplished in various ways. The gas may be applied direct or it may be done by electrolyzing the solution in the presence of matte: that is to say a fuse iron sulfid or a fused iron-copper sulfid, as obtained, for example, by fusing iron with sulfur, or in the smelting of low grade copper sulfid ore. Its derivation, however, is immaterial.

The acid in the electrolyte, acting on this material, produces hydrogen sulfid, which is immediately appropriated by the electrolyte, and by means of which the ferric sulfate is reduced. This may be represented by the equation:



and this hydrogen sulfid acts on the ferric sulfate according to equation 4. At the same time the copper and iron sulfids act directly and effectively on the ferric sulfate in the electrolyte, according to equations:



The copper sulfid is not as readily attacked as the iron sulfid, still, it does not do any harm in the electrolyte, and if it adheres to the cathode, in small amounts, it will be converted into the metal with the liberation of hydrogen and hydrogen sulfid.

After the ferric iron, or the variable valent salts, are reduced to their lowest valency the copper in the electrolyte would be attacked and precipitated. In small amounts the copper precipitate in the electrolyte is not particularly harmful. It is desirable to so regulate the process that all the variable valent salts will be reduced to their lowest valency, while no copper, or as little as possible, is precipitated. This is easily accomplished by regulating the flow of hydrogen sulfid, or if matte is used, by regulating its amount, the acidity of the electrolyte or the relative movement of the matte and electrolyte.

It will be noticed that the matte is not in electrical connection with the electrodes, and is used simply as a chemical reagent to reduce the variable valent salts, while electrolyzing the copper solution with insoluble electrodes.

If desired, both the liberated sulfur and the copper sulfid produced in the reactions, may be filtered from the electrolyte, but this will not ordinarily be necessary.

- 5 The effectiveness of the reactions, and the results obtained in the operation of the process, depend largely on the method of applying the hydrogen sulfid or its matte equivalent.
- 10 Referring to the accompanying drawings, Figure 1 represents a longitudinal section through an apparatus illustrating the process, in which hydrogen sulfid is used direct, and Fig. 2 the corresponding plan. Fig. 3
- 15 represents a longitudinal section of a modified apparatus in which matte is used in the electrolyte to liberate hydrogen sulfid in the electrolyzer and to reduce the variable valent elements, as set forth in equations 5, 6, and 7.
- 20 In the figures, 1 is a tank containing the electrolyte, which may be presumed to be copper sulfate solution as obtained, say, from leaching copper ores, and necessarily containing soluble salts of iron. 2 are the
- 25 anodes, and 3 the cathodes. 4 is a frame having stirring bars, 5, interposed between the electrodes, preferably oscillating as a whole, and suspended from fixed pivotal points 6, and actuated by the mechanism 7.
- 30 In Figs. 1 and 2, 10 represents a mechanism, taken as a whole, by means of which hydrogen sulfid is brought into a minute state of subdivision, or atomized, in contact with the electrolyte, and consists, preferably,
- 35 of a tube 11, having perforated disks 12, and suspended within the tank and electrolyte by the shaft 13, from the ball bearings 14. This tube is made to revolve at a high speed, driven by the motor 16. The
- 40 hydrogen sulfid is preferably produced in the hydrogen sulfid generator 17, from iron sulfid and dilute sulfuric acid, and, by means of the compressor 18, is forced through the pipe 19 and into the atomizer
- 45 10. It is desirable to maintain a circulation of the electrolyte from one end of the electrolyzer to the other so as to thoroughly distribute the reduced solution; this is accomplished by withdrawing the electrolyte from
- 50 one end of the cell through the pipe 20, which delivers it to the bottom of the atomizer 10. The circulation is promoted by inserting the end of the gas pipe 19 into the end of the solution pipe 20, thus acting as
- 55 an ejector, and delivering both the solution and the gas into the bottom of the tube 11. As the gas and electrolyte rises through the tube it is violently agitated, atomized, and mixed by the rapidly revolving disks 12, and
- 60 the gas brought in intimate contact with the electrolyte. In this way it is quite possible to reduce the variable valent elements without precipitating, or materially precipitating, any of the copper as sulfid. If the gas
- 65 is in excess of that required under the con-

ditions to reduce the variable valent elements, copper will be precipitated, but the production of the hydrogen sulfid is easily regulated by the amount of acid allowed to flow on the iron sulfid in the hydrogen sulfid generator. Or, if the installation is a large one, the hydrogen sulfid may be pumped into a gasometer in the ordinary way, and the flow from the gasometer into the electrolyte regulated by a valve. The

70 idea being, to allow enough hydrogen sulfid to flow into the electrolyzed solution to completely reduce the variable valent elements, but not in excess so as to precipitate any of the copper, although, as already stated, a

75 small amount of copper sulfid in the electrolyte will do no harm and may be beneficial, as shown by equation 6. A small amount of the gas should be applied to a relatively large amount of the electrolyte.

80 It is desirable to bring a large volume of solution in contact with the gas for the reduction of the variable valent salts and then bring a large volume of the reduced solution in contact with the electrodes, and to prevent, as far as possible, the variable valent

85 elements from being re-oxidized to the higher valencies. By regulating the speed of rotation of the cylinder, the amount and dilution of the gas, and the volume of the electrolyte, the variable valent salts may be readily reduced and maintained reduced without

90 chemically precipitating an appreciable amount of the copper as the sulfid, with hydrogen sulfid.

The space over the atomizer 10, is hooded or inclosed, shown by 28, so as to collect the excess gas, which is then exhausted through the pipe 22, by means of the exhauster 21.

105 Usually all the gas introduced into the atomizer 10 will be consumed in acting on the electrolyte, but if there is an excess, it is likely to be disagreeable. In any event, it is preferably exhausted from the electrolyzer or from the atomizer and forced outside of

110 the building.

30 is a filter to prevent the sulfur and sulfid precipitate from getting to the electrodes if it is desired to exclude it.

In Fig. 3, instead of using the hydrogen sulfid direct, matte or fused iron sulfid is introduced into the electrolyte. This may be effectively accomplished by circulating the electrolyte through the matte or by moving

115 the matte through the electrolyte. The result in either case, is much the same. The perforated anodes 2, bolted to the bars 36, are suspended from cross pieces 23 and 26, and from flexible suspenders 25, and oscillated by the mechanism 7. The matte 32 is

120 placed on the top of the anodes and moves with the anodes through the electrolyte. The action is further promoted by having chambers 31 at the ends of the electrolyzer filled with matte 32, through which the elec-

125 130

trolyte is circulated to and from the electrodes. The filter 30 prevents precipitate and insoluble matter from the matte from getting to the electrodes. 37 is a pump, by means of which the electrolyte is circulated. The electrolyte, flowing out of outlet 34, into the pipe 35 is elevated by pump 37 and returned to the electrolyzer through the pipe 33.

It will be noted that the matte is not electrically connected with the electrodes, nor is it directly electrolyzed, but is used primarily to maintain the variable valent salts at their lowest valency in the electrolysis of copper solution.

Hydrogen sulfid presents peculiar advantages in the electrolysis of impure copper solutions, due largely to its quick and effective action, care, however, must be exercised in applying it, for it is an energetic precipitant of the copper, and if the copper is chemically precipitated by the hydrogen sulfid, it not only makes useless electrolytic precipitation, but practically nullifies it. It is probably for this reason that its use as an effective reducing agent in the electrolysis of impure copper solutions has hitherto been unsuspected. It is vastly superior to sulfur dioxide, and numerous demonstrations show that hydrogen sulfid is effective in solutions where sulfur dioxide fails to show any appreciable advantage.

It is well known that sulfur dioxide is generally regarded as an effective reducing agent for the iron in the electrolysis of copper solutions. I have not found it so under all conditions when practically applied, even if applied to saturation. The action does not appear to be quick enough. In this respect hydrogen sulfid presents decided advantages. The action is almost instantaneous, but care must be taken to apply it in the proper amount and in a finely divided state of subdivision, so that the variable valent salts are reduced in large volumes of the electrolyte without appreciably precipitating any copper, as would be the case if this precaution were not taken.

I claim:

1. In the electrolysis of impure copper solutions the process which consists in continuously applying hydrogen sulfid to the solution to maintain the iron in the ferrous condition.

2. In the electrolysis of copper solutions containing salts of variable valent metals, the process which consists in applying hydrogen sulfid to the solution to maintain the salts of variable valent metals at their lowest valency.

3. A process which consists in electrolyzing a copper solution containing iron salts and continuously introducing hydrogen sulfid into the solution.

4. A process of electrolyzing copper sul-

fate solutions containing ferrous sulfate which consists in applying hydrogen sulfid to the electrolyte to maintain the iron in the ferrous condition.

5. A process which consists in electrolyzing a copper sulfate solution containing ferrous sulfate, whereby copper is deposited at the cathode and the ferrous salts converted to ferric salts at the anode, and applying hydrogen sulfid to the electrolyte to reduce the ferric salts to the ferrous salts.

6. A process which consists in electrolyzing a metal solution to deposit the metal and liberate a gas at the anode capable of converting ferrous salts to ferric salts, and applying hydrogen sulfid to the solution to maintain the iron in the ferrous condition.

7. A process of electrolyzing salts of a polybasic acid which consists in maintaining the salts of the variable valent metals at their lowest valency by means of hydrogen sulfid.

8. A process of electrolyzing copper sulfate solutions containing ferrous sulfate which consists in applying hydrogen sulfid to the electrolyte in amounts sufficient to reduce the ferric salts formed by the electrolytic action to the ferrous salts, but not in amounts sufficient to perceptibly precipitate the copper as sulfid.

9. In the electrolysis of copper sulfate solutions the process which consists in applying hydrogen sulfid to the electrolyte.

10. In the electrolysis of copper solutions containing salts of iron the process which consists in applying hydrogen sulfid to the solution to maintain the iron in the ferrous condition, and separating the sulfur liberated by the reaction from the solution.

11. The process of electrolyzing copper solutions containing salts of iron which consists in agitating the electrolyte, continuously applying hydrogen sulfid to the solution in a finely divided condition to maintain the iron in the ferrous condition, and catching the excess gas and conducting it away from the electrolyzer.

12. In the electrolysis of impure copper solutions the process which consists in agitating the electrolyte and continuously applying hydrogen sulfid to the solution to maintain the variable valent elements at their lowest valency.

13. In the electrolysis of copper solutions the process which consists in agitating the electrolyte, continuously applying hydrogen sulfid to the solution, and atomizing the hydrogen sulfid in contact with the solution.

14. In the electrolysis of copper solutions containing salts of iron, the process which consists in applying hydrogen sulfid to the solution and filtering the resulting sulfur and sulfid precipitate from the solution.

15. In the electrolysis of impure copper solutions the process which consists in agi-

tating the electrolyte, continuously applying hydrogen sulfid to the solution, and circulating the electrolyte.

5 16. An electrolytic process which consists in applying a sulfid reducing agent to the electrolyte to reduce and maintain reduced the variable valent salts in the electrolyte, said sulfid reducing agent not being electrically connected with the electrodes.

10 17. An electrolytic process which consists in applying a sulfid reducing agent to the electrolyte in a finely divided condition, to reduce and maintain reduced the variable valent salts in the electrolyte, and agitating the finely divided sulfid reducing agent in
15 contact with the electrolyte.

18. In the electrolysis of copper solutions containing salts of iron the process which consists in segregating a portion of the electrolyte from the electrodes, applying to the
20 segregated electrolyte a finely divided sulfid reducing agent, agitating the finely divided sulfid reducing agent in contact with the segregated electrolyte, filtering or separating the insoluble matter from the segregated
25 electrolyte, and returning the segregated filtered electrolyte to the electrodes.

19. An electrolytic process which consists in introducing hydrogen sulfid into the electrolyte, and then atomizing it in contact with
30 the electrolyte.

20. An electrolytic process which consists in applying a finely divided sulfid reducing agent to the electrolyte and agitating the
35 finely divided sulfid reducing agent in contact with the electrolyte.

21. In the electrolysis of copper solutions containing salts of iron, the process which consists in applying hydrogen sulfid to the solution and then electrolyzing the reduced
40 solution in the presence of a sulfid reducing agent.

22. A process of electrolyzing a solution of salts of a polybasic acid containing salts of the variable valent elements which consists in maintaining the salts of the variable
45 valent elements at their lowest valency by means of a sulfid reducing agent in the electrolyte not electrically connected with the electrodes.

23. A process of electrolyzing a solution of salts of a polybasic acid containing salts of the variable valent elements which consists in maintaining the salts of the variable
50 valent elements at their lowest valency by agitating a finely divided sulfid reducing agent in the electrolyte.

24. In the electrolysis of copper solution containing salts of the variable valent elements the process which consists in applying
60 a finely divided sulfid reducing agent to the solution, agitating the finely divided sulfid reducing agent in contact with the solution to reduce the variable valent salts in the electrolyte to their lowest valency, and
65 electrolyzing the reduced solution in the presence of a finely divided sulfid reducing agent.

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Witnesses:

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