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"IMPROVEMENTS IN OR RELATING TO THE ELECTROGALVANIZATION OF STEEL WIRES.

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This is an invention by HANDAY VENKATAKRISHNA UDUPA, Director, RAMASWAMY THANGAPPAN NADAR, Scientist and SARANGAPANI KRISHNAMURTHI, senior Scientific Assistant, all of Central Electrochemical Research Institute, Karaikudi Tamil Nadu, India, all Indians.

PROVISIONAL

The following specification describes the nature of this invention :

This invention relates to improvement in or relating to the electro-galvanization of steel wires of different gauges for use as fencing wire, telegraph wire and for making wire ropes and other commercial products.

Hitherto it has been proposed to electro-galvanize steel wires by using stationary electrolyte with or without stirring, or circulating the electrolyte in horizontal cells. Special addition agents are incorporated in the bath in order to obtain a satisfactory coating. Current densities normally employed are of the range 25 to 200 amp/dm².

This is open to the objection that very high current densities could not be employed, the thickness of the deposit is not uniform throughout ; and the requirement of the floor space for the unit is very large. Addition agents, if incorporated, are to be closely controlled within certain limits and in that case electrolyte purification is an additional operation.

The object of this invention is to obviate these disadvantages by employing fluidized bed technique wherein the steel wires which are to be galvanized are moved through a bed of inert particles fluidized by the flowing electrolyte as well as by employing forced circulation of the electrolyte in a vertical cylindrical column.

To these ends, the invention broadly consists in the electro-deposition of zinc from an aqueous bath of zinc sulphate (300 to 450 g/l) and sulphuric acid (25 to 100 g/l), on to moving steel wires, the electrolyte being kept under forced circulation or a fluidized bed of inert silica sand, quartz or glass beads of suitable particle size being maintained by the electrolyte. The above said process of electrogalvanization is carried out in a vertical cylindrical column-cum electrolyzer wherein the steel wire (cathode) which has undergone alkali and acid treatment is kept moving at desired speeds between 5 and 75 m/mt. The movement of the wires could be either in the vertical direction in the case of a deep cylindrical column or serpentine in shallow cylindrical column. The electrical connection to the cathode (moving wire) is given at multi points. The anodes, zinc or lead-silver alloy, are placed in position facing the moving cathode wires. Maximum cathode current densities 300 and 500 amp/dm² are employed in forced circulation and fluidized bed systems respectively. The temperature is maintained at desired values between 30 and 65°C. While using insoluble anodes, the replenishment of zinc in the bath is done by passing the weak electrolyte through a column packed with scraps, bars, strips or plates of zinc. In order to prevent excessive electrolyte spray during plating operation, heavy frothing is maintained on the top of the galvanizing column by adding small amounts of a mixture of silicic and cresylic acid to the electrolyte.

The following typical examples are given to illustrate the invention :

Example 1A

ELECTROGALVANIZATION OF STEEL WIRE IN AN INERT FLUIDIZED BED

Details of the fluidizing column-cum-galvanizer	: Cylindrical PVC column (10 cm dia×40cm height)
Fluidized material and average particle diameter	: Silica sand of average particle dia 0.390 mm
Electrolyte	: Aqueous solution of zinc sulphate (404 g/l) and sulphuric acid (60 g/l)
Linear velocity of electrolyte based on empty cross-section of the column	: 1.01 cm/sec.
Electrolyte temperature	: 45±5°C
Anode	: Lead-silver alloy
Cathode	: Moving steel wire (22 Swg)
Speed of the wire	: 13.2 m/mt
Current passed	: 42 amps
Cathode current density	: 500 amp/dm²
Cell voltage	: 13·2 to 13 6 volts
Duration of the experimental run	: 40 minutes
Weight of zinc deposited	: 33.55g.
Cathode current efficiency	: 97.8%
Thickness of the deposit	: 4 25 micron
Nature of the deposit	: Bright, smooth, uniform and very adherent.

Example 1B

ELECTROGALVANIZATION OF STEEL WIRE WITH FORCED CIRCULATION OF ELECTROLYTE

Details of the column-cum-galvanizer	: Cylindrical PVC column (10 cm dia×40cm ht.)
Electrolyte	: Aqueous solution of zinc sulphate (404 g/l) and sulphuric acid (60 g/l)
Linear velocity of electrolyte	: 4·04 cm/sec.
Electrolyte temperature	: 40±5°C
Anode	: Lead-silver alloy
Cathode	: Moving steel wire (22 Swg)
Speed of the wire	: 8·3 m/mt
Current passed	: 25 amps
Cathode current density	: 300 amp/dm²
Cell voltage	: 6.6—7.1 volts
Duration of experimental run	: 40 minutes
Weight of zinc deposited	: 19.93 g.
Cathode current efficiency	: 97%
Thickness of the deposit	: 4.0 micron

Price : Rs. Two Only.

Nature of the deposit	: Bright, smooth, uniform and very adherent

Example IIA

ELECTROGALVANIZATION OF STEEL WIRE IN AN INERT FLUIDIZED BED

Details of the fluidizing column-cum-galvanizer	: Cylindrical PVC column (10cm dia × 40cm height)
Fluidized material and average particle diameter	: Silica sand of average particle diameter : 0.296 mm
Electrolyte	: Aqueous solution of zinc sulphate (394 g/l) and sulphuric acid (54 g/l)
Linear velocity of electrolyte based on empty cross section of the column	: 0.81 cm/sec.
Electrolyte temperature	: 45±5°C
Anode	: Zinc
Cathode	: Moving steel wire (24 Swg)
Speed of the wire	: 9.2 m/mt
Current passed	: 34.5 amps
Cathode current density	: 500 amp/dm²
Cell voltage	: 7.5 to 7.8 volts
Duration of the experimental run	: 30 mts.
Weight of zinc deposited	: 20.37 g.
Cathode current efficiency	: 96.8%
Thickness of the deposit	: 6 micron
Nature of the deposit	: Bright, smooth, uniform and very adherent

Example IIB

ELECTROGALVANIZATION OF STEEL WIRE WITH FORCED CIRCULATION OF ELECTROLYTE

Details of the column-cum-galvanizer	: Cylindrical PVC column (10cm dia. × 40cm ht)
Electrolyte	: Aqueous solution of zinc sulphate (394 g/l) and sulphuric acid (54 g/l)
Linear velocity of electrolyte	: 4 cm/sec.
Electrolyte temperature	: 40±5°C
Anode	: zinc
Cathode	: Moving steel wire (24 SWG)
Speed of the wire	: 5.45 m/mt
Current passed	: 21 amps
Cathode current density	: 300 amp/dm²
Cell voltage	: 3.4 to 4 volts
Duration of the experimental run	: 30 mts.
Weight of zinc deposited	: 12.46 g.
Cathode current efficiency	: 97%
Thickness of the deposit	: 6.2 micron
Nature of the deposit	: Bright, smooth, uniform and very adherent

The following are among the main advantages of the invention :

(1) By employing the above said techniques along with the composition and other operating conditions of the bath mentioned in the examples, current densities of 300 to 500 amp/dm² could be employed.

(2) These processes of deposition avoid the use of special addition agent which are costly.

(3) The coatings of zinc obtained by the aforesaid methods are bright, smooth and uniform and very adherent to the base metal and these galvanized wires are suitable for use as fencing wire, telegraph wire etc., and for making wire ropes and other commercial products.

(4) The floor space requirement is considerably reduced due to the use of vertical columns instead of long horizontal galvanizers.

Dated this 4th day of November, 1970.

COMPLETE

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :

This invention relates to IMPROVEMENTS IN OR RELATING TO THE ELECTROGALVANIZATION OF STEEL WIRES IN AN INERT FLUIDIZED BED AND IN ELECTROLYTE UNDER FORCED CIRCULATION.

This invention relates more particularly to improvements in or relating to the electro-galvanization of steel wires of different gauges for use as fencing wire, telegraph wire and for making wire ropes and other commercial products.

Hitherto it has been proposed to electro-galvanize steel wires by using stationary electrolyte with or without stirring, or circulating the electrolyte in horizontal cells. Special addition agents are incorporated in the bath in order to obtain a satisfactory coating. Current densities normally employed are of the range of 25 to 200 amp/dm².

These are open to the objection that very high current densities could not be employed, the thickness of the deposit is not uniform throughout ; and the requirement of the floor space for the unit is very large. Additional agents, if incorporated, are to be closely controlled within certain limits and in that case electrolyte purification is an additional operation.

The main object of this invention is to get bright uniform and adherent deposit of zinc at very high current densities on moving wires of steel for use as fencing wire, telegraph wire and for making wire ropes and other commercial products.

The new principle underlying the invention is the employment of fluidized bed technique as well as forced circulation of electrolyte wherein the moving steel wire is surrounded by a bed of inert particles fluidized by an acid type electrolyte kept under normal speed of circulation for fluidized bed or under very high speed of forced circulation without fluidized bed.

The zinc deposited as described above is bright in appearance and was continuous and uniform throughout as it could withstand, without failure, a number of immersions varying from ½ to 3 in saturated copper sulphate solution (360 g. of $CuSO_4.5H_2O$ in one litre of distilled water), depending on the mass of zinc deposited per unit area (40 to 250 g/m²). The zinc coating is also adherent to the basis steel wire as the coating showed no sign of peeling or cracks when it is wound round a cylindrical mandrel so as to form ten close spirals, the diameter of the mandrel being dependent on the diameter of the wire (the ratio between the diameter of mandrel and of the wire varies from 2 to 6).

According to the present invention there is provided a process for the electrodeposition of zinc from an aqueous bath of zinc sulphate (300 to 450 g/l) and sulphuric acid (25 to 100 g/l), on to moving steel wires, the electrolyte being kept under forced circulation or a fluidized bed of inert particles being maintained by the electrolyte, the wire being moved at desired values between 5 and 75 m/mt, the cathodic current density being maintained at a value of 300 to 500 amp/dm² and the temperature of the electrolyte being maintained at 30–65°C.

The present invention constitutes an improvement in the process of coating of zinc from an aqueous bath of zinc sulphate (300 to 450 g/l) and sulphuric acid (25 to 100 g/l), on to moving steel wires, the electrolyte being kept under forced circulation or a fluidized bed of inert silica sand, quartz or glass beads of suitable particle size being maintained by the electrolyte. The above said process of electrogalvanization is carried out in a vertical cylindrical column-cum-electrolyzer wherein the steel wire (cathode) which has undergone acid treatment is kept moving at desired speeds between 5 and 75 m/mt. The movement of the wires could be either in the vertical direction in the case of a deep cylindrical column or serpentine in shallow cylindrical column. The electrical connection to the cathode (moving wire) is given at multi points. The anodes, zinc or lead-silver alloy (1% silver) are placed in position facing the moving cathode wires. Maximum cathode current densities 300 and 500 amp/dm² are employed in forced circulation and fluidized bed systems respectively. The temperature is maintained at desired values between 30 and 65°C. While using insoluble anodes, the replenishment of zinc in the bath is done by passing the weak electrolyte through a column packed with scraps, bars, strips or plates of zinc. In order to prevent excessive electrolyte spray during plating operation, heavy frothing is maintained on the top of the galvanizing column by adding small amounts of a mixture of silicic and cresylic acid to the electrolyte. Due to the employment of high current densities, the production capacity increased and the production cost is reduced.

Another novel feature of the invention is the use of vertical cylindrical fluidizing column-cum-galvanizer instead of the conventional horizontal rectangular galvanizer which is quite long and occupies much larger space.

The flow sheet of the process is given in Fig. 1 of the accompanying drawings. The uncoiled (1) wire is pickled in hydrochloric acid (2), rinsed with water (3), etched anodically (4) in sulphuric acid and again rinsed with water (5). This pretreated wire is taken through the vertical galvanizer (6) when it gets coated with zinc. This galvanized wire leaving to column is rinsed with water (7) and dipped in chromate solution (8), if required, water rinsed (9), air dried (10) and coiled (11). Either forced circulation of electrolyte or fluidized bed is maintained inside the galvanizer. The replenishment of the electrolyte (while using insoluble anode) is done by passing the depleted electrolyte through the column (12) packed with zinc plates or scraps. The electrolyte received in the circulation tank (13) is circulated by means of the circulating pump (14).

EXAMPLES :

Example I A

ELECTROGALVANIZATION OF STEEL WIRE IN AN INERT FLUIDIZED BED

Details of fluidizing column-cum-galvanizer	: Cylindrical PVC column (10 cm dia × 40cm height)
Fluidized material and average particle diameter	: Silica sand of average particle dia 0.390 mm
Electrolyte	: Aqueous solution of zinc sulphate (404 g/l) and sulphuric acid (60 g/l)
Linear velocity of electrolyte based on empty cross-section of the column.	: 1.01 cm/sec.
Electrolyte temperature	: 45±5°C
Anode	: Lead-silver alloy
Cathode	: Moving steel wire (22 SWG)
Speed of the wire	: 13.2 m/mt
Current passed	: 42 amps
Cathode current density	: 500 amp/dm²
Cell voltage	: 13·2 to 13·6 volts
Duration of the experimental run	: 40 minutes
Weight of zinc deposited	: 33.55g.
Cathode current efficiency	: 97.8%
Thickness of the deposit	: 4.25 micron
Nature of the deposit	: Bright, smooth, uniform and very adherent.

Example I B

ELECTROGALVANIZATION OF STEEL WIRE WITH FORCED CIRCULATION OF ELECTROLYTE

Details of the column-cum-galvanizer	: Cylindrical PVC column (10 cm dia × 40cm ht.)
Electrolyte	: Aqueous solution of zinc sulphate (404 g/l) and sulphuric acid (60 g/l)
Linear velocity of electrolyte	: 4·04 cm/sec.
Electrolyte temperature	: 40±5°C
Anode	: Lead-silver alloy
Cathode	: Moving steel wire (22 SWG)
Speed of the wire	: 8·3 m/mt
Current passed	: 25 amps
Cathode current density	: 300 amp/dm²
Cell voltage	: 6.6—7.1 volts
Duration of experimental run	: 40 minutes
Weight of zinc deposited	: 19.93 g.
Cathodic current density	: 97%
Thickness of the deposit	: 4.0 micron
Nature of the deposit	: Bright, smooth, uniform and very adherent

Example II A

ELECTROGALVANIZATION OF STEEL WIRE IN AN INERT FLUIDIZED BED

Details of the fluidizing column-cum-galvanizer	: Cylindrical PVC column (10cm dia × 40cm height)
Fluidized material and average particle diameter	: Silica sand of average particle diameter : 0.296
Electrolyte	: Aqueous solution of zinc sulphate (394 g/l) and sulphuric acid (54 g/l)
Linear velocity of electrolyte based on empty cross section of the column	: 0.81 cm/sec.
Electrolyte temperature	: 45±5°C
Anode	: Zinc
Cathode	: Moving steel wire (24 SWG)
Speed of the wire	: 9.2 m/mt
Current passed	: 34.5 amps
Cathode current density	: 500 amp/dm²
Cell voltage	: 7.5 to 7.8 volts
Duration of the experimental run	: 30 mts.
Weight of zinc deposited	: 20.37 g.
Cathode current efficiency	: 96.8%
Thickness of the deposit	: 6 micron
Nature of the deposit	: Bright, smooth, uniform and very adherent

Example II B

ELECTROGALVANIZATION OF STEEL WIRE WITH FORCED CIRCULATION OF ELECTROLYTE

Details of the column-cum-galvanizer	: Cylindrical PVC column (10cm dia. × 40cm ht.)
Electrolyte	: Aqueous solution of zinc sulphate (394 g/l) and sulphuric acid (54 g/l)
Linear velocity of electrolyte	: 4 cm/sec.
Electrolyte temperature	: 40±5°C
Anode	: zinc
Cathode	: Moving steel wire (24 SWG)
Speed of the wire	: 5.45 m/mt
Current passed	: 21 amps
Cathode current density	: 300 amp/dm²
Cell voltage	: 3.4 to 4 volts
Duration of the experimental run	: 30 mts.
Weight of zinc deposited	: 12.46 g.
Cathode current efficiency	: 97%

Thickness of the deposit	: 6.2 micron
Nature of the deposit	: Bright, smooth, uniform and very adherent

The advantages of the invention are :

(1) By employing the above said techniques along with the composition and other operating conditions of the bath mentioned in the examples, current densities of 300 to 500 amp/dm² could be employed.

(2) These processes of deposition avoid the use of special addition agent which are costly.

(3) The coatings of zinc obtained by the aforesaid methods are bright, smooth and uniform and very adherent to the base metal and these galvanized wires are suitable for use as fencing wire, telegraph wire etc., and for making wire ropes and other commercial products.

(4) The floor space requirement is considerably reduced due to the use of vertical columns instead of long horizontal galvanizers.

Summarising, the present invention affords a convenient method for obtaining bright, uniform and adherent deposit of zinc from acid type baths at very high current densities on moving wires of steel. This does not involve the use of addition agent. The effect may be attributed to the intense turbulence and interfacial agitation created by the fluid under forced circulation or fluidized bed.

WE CLAIM

(1) A process for the electrode position of zinc from an aqueous bath of zinc sulphate (300 to 450 g/l) and sulphuric acid (25 to 100 g/l), on to moving steel wires, the electrolyte being kept under forced circulation or a fluidized bed of inert particles being maintained by the electrolyte, the wire being moved at desired values between 5 and 75 m/mt, the cathodic current density being maintained at a value of 300 to 500 amp/dm² and the temperature of the electrolyte being maintained at 30–65°C.

(2) A process as claimed in claim (1) wherein the electrode position of zinc is carried out in the electrolyte under forced circulation or in the presence of a fluidized bed of inert particles like silica sand, quartz or glassbeads, fluidized by the flowing electrolyte.

(3) A process as claimed in claim 1 or 2 wherein the galvanization operation is carried out in a vertical cylindrical column.

(4) A process as claimed in the preceding claims whereby bright, uniform and adherent deposit of zinc on steel wires is obtained.

(5) A process for the electrogalvanization of moving steel wires, substantially as described hereinbefore in the examples and Fig. 1.

Dated this 15th day of July, 1971.

Sd.

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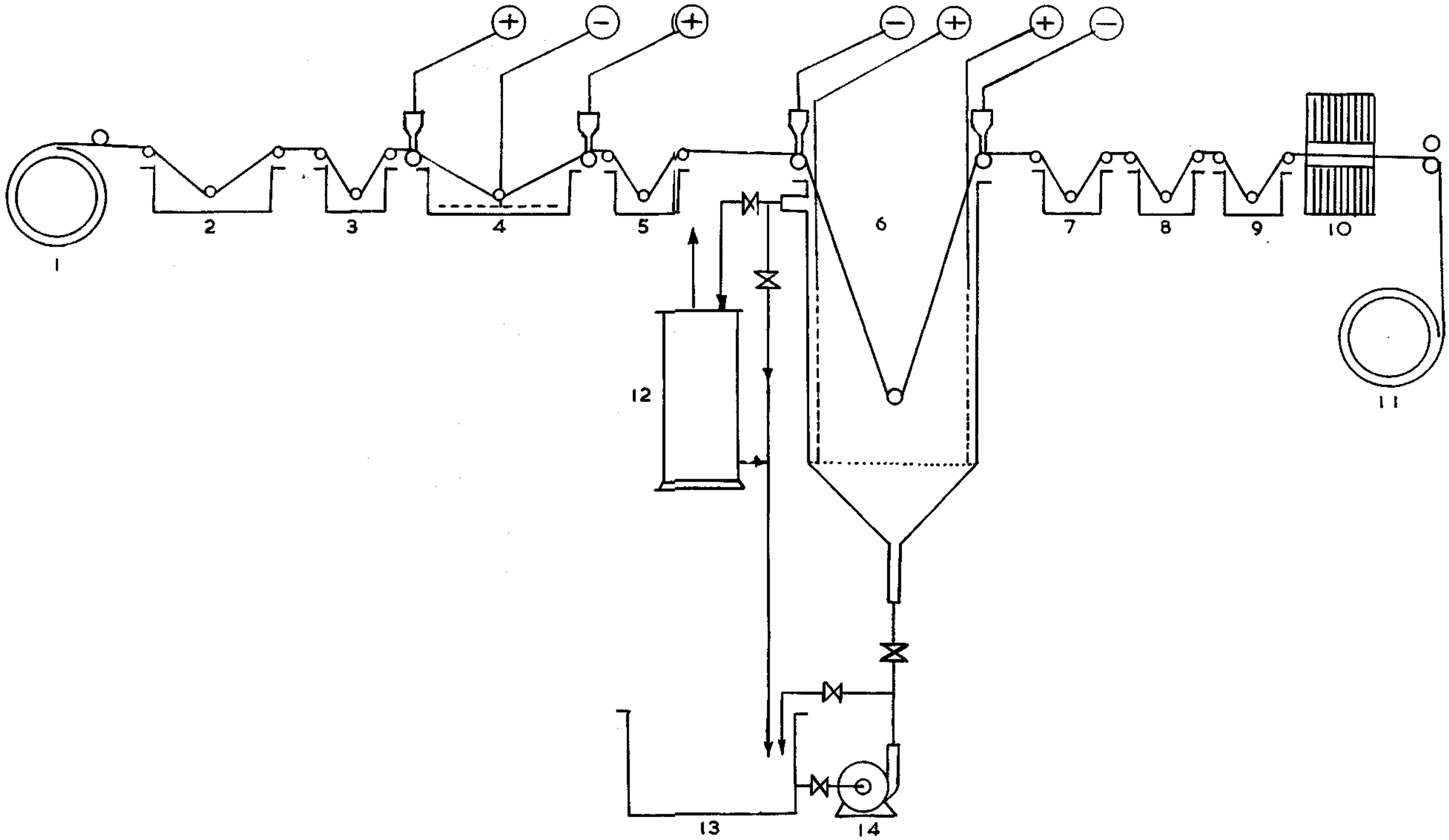

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