

PATENT SPECIFICATION (11) 1 412 545

1 412 545
(21) Application No. 37492/73 (22) Filed 7 Aug 1973
(44) Complete Specification Published 5 Nov 1975
(51) INT CL² C03B 5/16
(52) Index at acceptance
C1M 11A2 11D1 11D6
(72) Inventors: MICHAEL BRUNGS, JOHN BURNISTON



(54) "GLASS COLOUR CHANGES"

(71) WE, A.C.I. OPERATIONS PTY. LIMITED, a Company Incorporated under the laws of the State of Victoria of 550 Bourke Street, Melbourne, State of 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:

The present invention relates to methods for changing the colour of glass melt in a glass furnace.

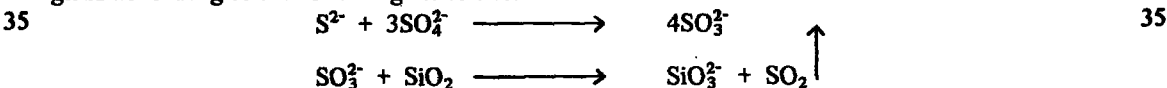
Often, the particular colour of a glass melt is associated with a particular range of oxidation state in the melt that is compatible with that colour. Hence, in such cases to change the colour of the melt it is also necessary to change its oxidation state.

The oxidation state of a glass is related to the partial pressure of oxygen within the glass. Since it is difficult to measure the dissolved oxygen content of a glass, the oxidation state of a glass is often estimated from the constituents of the batch from which it is made, and glass oxidation state is defined in terms of an empirical factor known as the Manning Carbon Number (Glass Ind. 39, (3), 139, 1958). The method of determining "Carbon Number" assumes that all reducing and oxidising agents in the glass batch can be given a number which equates their reducing or oxidising power to a certain number of ounces of carbon (which may be positive or negative) in a batch weight normalised to 2000 lb. of sand. In this way the effect of including a variety of these materials in a batch can be found by adding their carbon numbers to give the resultant level of oxidation or reduction in the glass. Using this system, an oxidising glass has a carbon number less than -20 depending upon the nature of the furnace atmosphere.

Foam formation occurs when glass melts of different oxidation state are mixed, and since the foam reduces heat transfer in the melt and causes gas inclusions known as seed and blister to appear in the final manufactured glass, it is necessary to effect such colour changes in such a way as to minimise foam formation.

Hitherto, such colour changes have been effected using a run-out/flush/fill-on technique. As the name suggests, this procedure involves running out or draining most of the molten glass from the furnace, and displacing or "flushing" the remaining glass in the furnace with glass of incoming colour. The furnace is then filled with batch and cullet appropriate to the new colour. In this way foam formation is minimised, though the technique is a very lengthy one, often taking between eighty and nine-six hours to complete.

It is thought that foam formation results from the reaction of sulphide with sulphate in the glass according to the following reactions:—



Gas evolution is accentuated by the fact that as the glass passes from one oxidation state to another, solubility of the gases present in the glass passes through a minimum. That is, the SO₂ formed as a result of the sulphide/sulphate interaction is unable to dissolve in the glassy matrix and, hence, is released as gas bubbles which rise to the glass surface. (See Manning, W. H., Billings, D. B., Conroy, A.R., Bauer, W. C. "Reduced sulphur compounds" Glass Ind. July 1967, p 374).

As glass manufacturers are often committed to numerous colour changes each year, and many such changes involve a change in oxidation state of the melt, the loss of productivity caused by foaming during colour changes can be quite large.

The present invention provides a method of reducing foam formation in glass furnaces which occurs during colour changes involving changes of the oxidation state of the glass melt. The method of the present invention of changing colour between glass melts of different oxidation state results in less loss of saleable glass production than the conventional run-out/flush/fill-on procedure.

Applicants have found that foaming during such colour changes can be reduced by adjusting the oxidation state of the melt in the furnace (e.g. by varying the composition of the batch being added to the said melt) so that the difference in the oxidation state of the melt in the furnace and that of the incoming second melt or batch of the new colour is reduced. This results in a decrease in inter-chemical reaction between the second colour and first colour melts thereby reducing formation of gaseous sulphur dioxide. Such an adjustment is suitable for use in colour change methods involving a run-out/fill-on technique or a transition technique.

In the run-out/fill-on type of colour change, the need for a flush step can often be eliminated because of the reduction in foam formation.

Alternatively, in what is known as a transition colour change, the composition, colour and oxidation state of the melt furnace can be adjusted to the required levels for the differently coloured incoming melt without having substantially to alter the level of melt in the furnace at any given time. Hence in the transition change, it is possible continuously to change the oxidation state of the glass melt in the furnace by adjusting the constituents of the incoming batch which affect oxidation state. When the oxidation state of the melt in the furnace has been adjusted as closely as possible to that of the required new melt, addition of colouring ingredients for the new melt may then be commenced. The actual composition of the first or outgoing melt only taking into account the major constituents of the said melt (i.e. excluding the small amounts of constituents which affect colour and oxidation state) should also be altered to correspond to that of the second or incoming melt at any stage during the change-over by appropriate adjustment of the major constituents in the incoming batch. At the same time as batch comes in, glass melt is withdrawn from the furnace to be formed into finished glassware. Hence, the level of the glass melt in the furnace remains substantially constant while its composition, colour and oxidation state are being altered by the addition of bath.

Accordingly the present invention provides a method of reducing foam formation which occurs in a furnace during changeover from a first to a second glass melt of different oxidation state as hereinbefore defined and colour which comprises adjusting the oxidation state of the first melt towards that of the second melt by addition or removal of oxidising or reducing agents from the melt prior to introducing or removing colourants in order to produce the color of the second melt.

The maximum rate at which the oxidation state of the first melt is adjusted is governed by the residence time distribution in a particular furnace, i.e. the effect of capacity and physical dimensions of a furnace will affect the rate of batch additions because a batch will usually appear in the furnace output at any time between 8 and 48 hours after addition depending on the furnace and the rate at which glass is being drawn. Discussions of these factors can be found in most chemical engineering text e.g. Chemical Reaction Engineering by Octave Levenspiel % Second Printing. Hence the maximum rate of additions possible while the oxidation state is being varied can be readily determined by the person skilled in the art by calculation and experiment and requires no further explanation herein.

The oxidation state of the first melt is adjusted towards that of the second melt by varying the concentration of the oxidation and/or reducing agents in the incoming batch fed to the melt thereby to adjust the concentration of the agents in the melt. Examples of suitable oxidising agents are dichromates, arsenic, sodium sulphate, gypsum, barytes and nitre and preferred reducing agents include slag, aluminium powder, cyanides, carbon, sulphur, calcium sulphide, ferrous sulphide, iron pyrites and iron chromite. However, any other conventional oxidising or reducing agents compatible with the glass melt may also be suitable.

To minimise foam formation in a transition type change it is preferred that the oxidation state of the first melt be adjusted as closely as possible to that of the second melt without causing colour instability of the melt. However, such careful adjustment is generally not necessary for a run-out/fill-on type of change.

A glass melt is defined as having colour instability when small changes of glass oxidation state of the melt give large changes in colour of the melt. For example the transmission of the melt for a major absorption band may change by at least 10% with a change of about 10 units in the carbon number of the melt.

The method of the invention helps to reduce the amount of foam produced during the changeover thereby permitting a more rapid colour change. However, some foam formation will almost inevitably occur even though the actual amount of foaming is reduced. Spraying the foam with oil using conventional techniques further reduces the remaining foam if this is necessary. Such a technique is described in U.U Patent No. 3,350,185 to Owens Illinois Inc.

Using the applicants' method it is often possible to eliminate the need for a "flush" step if a run-out/fill-on type of colour change is carried out. The time and materials saved by eliminating the flush step makes the applicants' invention less costly than the conventional run-out/flush/fill-on techniques.

5 However, in some instances, the use of a run-out/fill-on technique is not possible because of the unacceptable strain this may place on an aged glass furnace. Alternatively it may not be possible to carry out such changes because of the lack of a reliable water supply or because of the physical limitations imposed by furnace construction. 5

10 Using the applicants' method it is often possible in such cases to effect a transition colour change which avoids the run-out/fill-on steps completely thereby reducing or eliminating the strain on the glass furnace. 10

Generally speaking, the applicants have found when using their method that foam is reduced by at least 30% and often by more than 50% in comparison with prior art colour change methods operated over the same length of time.

15 The following Examples illustrate preferred embodiments of the invention: 15

EXAMPLE 1

Transition from a reduced to an oxidation glass

The oxidation state and composition of a reduced amber glass melt were altered slowly by adjusting the major ingredients of the incoming batch until the melt composition corresponded to that of the proposed new melt. At the same time the amount of carbon in the incoming batch was reduced to make the amber glass melt more oxidised. The carbon numbers of the batch added to the melt at different stages of the changeover are summarised in Table A. Carbon "removal" was continued until a limiting amber composition was reached, that is until the glass colour started to become unstable. At this point the iron level in the incoming batch was increased sufficiently to maintain the amber colour. Once the limiting amber colour was reached the colour change was accomplished by filling on with oxidised glass batch and colourant without excessive foam formation. The foam was reduced at this stage by an oil spray applied to it. This method was used and found to be successful for amber glass to U.V. green glass transitions and also for amber glass to flint glass transitions. 20 However, it was found that foam formation was less for amber glass to U.V. green glass transitions than for amber glass to flint glass transitions because of the strongly oxidising nature of the high colourant batch used in the amber glass to U.V. green glass change. 25

TABLE A

Amber glass to U.V. green glass transition

35 Carbon Number 35
 —120 At the beginning of the changeover
 — 65 When addition of colourant commenced
 + 19 When the changeover was complete

Amber glass to flint glass transition

40 Carbon Number 40
 —120 At the beginning of the changeover
 — 65 When addition of colourant commenced
 + 8 When the changeover was complete

EXAMPLE 2

Transition from an oxidised to a reduced glass

Applicants have found that such changes must normally be carried out slowly to avoid foaming problems. The present Example deals with a flint glass to amber glass transition. 45

A flint glass melt was gradually reduced as much as possible by lowering or eliminating the oxidants, arsenic oxide and sodium nitrate, from the incoming batch. The carbon numbers of the batch added to the melt at different stages of the changeover are summarised in Table B. 50 The reducing agent carbon was also added to the batch to reduced the glass melt further. Thereafter sufficient iron oxide was added to develop an amber colour. In this way it was possible to pass slowly through the "foaming region" whilst minimising the production of off-colour ware. Development of the amber colour took approximately ninety-six hours from the start of the change. However, only thirty-six to forty-eight hours of the ware produced was considered "off colour" and all but ten hours of production was saleable. By reducing the white glass as far as possible before adding the iron oxide required to develop an amber colour the production of off-colour ware was minimised. During the colour change some foam was produced in the tank. However, the foam level never exceeded two inches and was therefore of no real consequence despite the fact that it did cause a slight drop in bottom temperatures. 55 60

TABLE B

Carbon Number
 + 8 At the beginning of the changeover
 — 25 When addition of colourant commenced
 65 —120 When the changeover was complete 65

EXAMPLE 3

Run-out colour change of production of a reduced glass (amber glass) after an oxidised glass (flint glass)

As mentioned previously, the traditional run-out/flush/fill-on colour changes can take anything from eighty to ninety-six hours to complete. The present Example deals with a run-out flint glass to amber glass change which can be completed within twenty-four hours. Part of the reason for the speed of the change is that a flush out step is not required.

To minimise the amount of foam formed when amber cullet was batched into the flint glass remaining in the tank, the flint glass was reduced prior to the colour change. Thus, the oxidants, arsenic oxide and sodium nitrate, were removed from the flint glass by lowering the amounts of these oxidants in the incoming batch, twenty-four hours before changeover. The reduced flint glass was then rapidly drained from the tank with the furnace being kept as hot as possible to ensure easy flow of the melt. Once tapped, the flint glass was run out at an average of 25 tons/hr., the actual run-out phase of the operation taking approximately six and a half hours. At the end of the run-out approximately four inches of flint glass remained in the tank. Amber cullet fill-on was then commenced at six tons per hour, cullet guns being used to distribute the cullet over the tank evenly. An oil spray and the pre-reduction of the flint glass were effective in reducing the amount of foam formed during fill-on. After two hours fill-on rate was increased to eight tons per hour and finally to ten tons per hour and finally to ten tons per hour. With the glass level five and a half inches down, amber batch fill-on was commenced. Batch was added at an average rate of six and a half tons per hour. This brought the tank on level twenty-three and a half hours after tapping. The first twenty batches (eleven used in fill-on) contained extra soda ash and 10% extra pyrites and coke to assist in color development. Colour was acceptable six hours after the fill-on had been completed. The carbon numbers of the batch added to the furnace at different stages of the changeover are summarised in Table C.

TABLE C

Carbon Number

+ 8 At the beginning of the changeover
— 5 Immediately prior to run-out
—120 Fill-on

EXAMPLE 4

Transition change from amber glass to white glass

This Example provides a detailed description of a stepwise change from amber glass to white glass at applicant's plant at Lae, New Guinea.

The steps are summarised in Table 1 and the levels of the added ingredients determining carbon number and colour (iron oxide) for the incoming batch are given in Table 2.

TABLE 1

STEP	CARBON NUMBER (CN)	PERIOD IN HOURS OVER WHICH THE BATCH WAS ADDED
0	-130	—
1	- 70	22
2	- 30	6
2A	- 10	7
3	+ 16	8
4	+ 24.5	24
5	+ 21.5	—

TABLE 2

STEP CHANGE SCHEDULE

	MATERIALS (DRY WEIGHTS IN LBS)	INITIAL	1	2	2A	3	4	
5	SALTCAKE (Na_2SO_4)	9.0	5	5	5	5	—	5
	GYPSUM	—	—	—	—	—	11	
10	SODIUM NITRATE	—	—	—	—	7	7	10
	IRON OXIDE	1.73	1.94	—	—	—	—	
	COAL DUST	5.8	3.5	2.5	1.25	—	—	
15	* CARBON NUMBER	—130	—70	—30	—10	+16	+24.5	15
	BATCH TIME (HOURS)	—	22	6	7	8	24	

20 *NOTE: C.N. of Amber cullet assumed to be —130 : C.N. of white cullet assumed to be +22. 20

25 Introduction of the CN —70 batch caused no foam problems at all. However, a little foam accompanied the introduction of the CN —30 batch, but not as much as anticipated. When the batch of CN —10 was introduced into the furnace the foam level rose to about 3 inches to 4 inches, but it was not until the introduction of the CN +16 batch that any great amount of foam was formed and a maximum foam level of 7 inches was reached 51 hours after the introduction of the first transition batch. This foam did not remain long and the majority had disappeared within 12 hours. With the rapid change in carbon number, the amber colour faded, thereby minimising the production of off-colour ware. 25

30 The above change gave satisfactory control of foam generation and a relatively short total time for the transition and the glassware produced from the melt was not affected by seed or blister for the whole period of the change. 30

WHAT WE CLAIM IS:

35 1. A method of reducing foam formation which occurs in a furnace during a changeover from a first to a second glass melt of different oxidation state as hereinbefore defined and colour which comprises adjusting the oxidation state of the first melt towards that of the second melt by addition or removal of oxidizing or reducing agents from the melt prior to introducing or removing colourants in order to produce the colour of the second melt. 35

40 2. A method according to claim 1 wherein the oxidation state of the first melt is adjusted towards that of the second melt until the first melt is on the verge of colour instability as hereinbefore defined. 40

45 3. A method according to claim 2 wherein the oxidation state of the first melt is adjusted towards that of the second melt to a point such that a change of 10 units in the carbon number as hereinbefore defined of the first melt results in a change of transmission of the first melt for a major absorption band of at least 10%. 45

50 4. A method according to claim 2 or 3 wherein colourant addition or removal is commenced after the first melt has reached the verge of colour instability. 50

55 5. A method according to any one of the preceding claims wherein the oxidation state of the first melt is adjusted by varying the concentration in the melt of at least one of the oxidizing substances comprising dichromates, arsenic, sodium sulphate, gypsum, barytes and nitre, and, or at least one of the reducing substances comprising slag, aluminium powder, cyanides, carbon, sulphur, calcium sulphide, ferrous sulphide, iron purites and iron chromite. 55

6. A method according to any one of the preceding claims wherein the level of the glass melt in the furnace is maintained substantially constant throughout the changeover.

7. A method according to any one of claims 1 to 5 which comprises running out the first melt from the furnace after its oxidation state has been adjusted and filling on the furnace with the second melt. 55

8. A method according to claim 1 substantially as hereinbefore described in any one of the foregoing Examples.

J. A. KEMP & CO.,

Chartered Patent Agents,

14 South Square,

Gray's Inn, LONDON WC1 5EU



TABLE 2

STEP CHANGE SCHEDULE

	MATERIALS (DRY WEIGHTS IN LBS)	INITIAL	1	2	2A	3	4	
5	SALTCAKE (Na_2SO_4)	9.0	5	5	5	5	—	5
	GYPSUM	—	—	—	—	—	11	
10	SODIUM NITRATE	—	—	—	—	7	7	10
	IRON OXIDE	1.73	1.94	—	—	—	—	
	COAL DUST	5.8	3.5	2.5	1.25	—	—	
15	* CARBON NUMBER	—130	—70	—30	—10	+16	+24.5	15
	BATCH TIME (HOURS)	—	22	6	7	8	24	

20 *NOTE: C.N. of Amber cullet assumed to be —130 : C.N. of white cullet assumed to be +22. 20

Introduction of the CN —70 batch caused no foam problems at all. However, a little foam accompanied the introduction of the CN —30 batch, but not as much as anticipated. When the batch of CN —10 was introduced into the furnace the foam level rose to about 3 inches to 4 inches, but it was not until the introduction of the CN +16 batch that any great amount of foam was formed and a maximum foam level of 7 inches was reached 51 hours after the introduction of the first transition batch. This foam did not remain long and the majority had disappeared within 12 hours. With the rapid change in carbon number, the amber colour faded, thereby minimising the production of off-colour ware. 25

The above change gave satisfactory control of foam generation and a relatively short total time for the transition and the glassware produced from the melt was not affected by seed or blister for the whole period of the change. 30

WHAT WE CLAIM IS:

1. A method of reducing foam formation which occurs in a furnace during a changeover from a first to a second glass melt of different oxidation state as hereinbefore defined and colour which comprises adjusting the oxidation state of the first melt towards that of the second melt by addition or removal of oxidizing or reducing agents from the melt prior to introducing or removing colourants in order to produce the colour of the second melt. 35

2. A method according to claim 1 wherein the oxidation state of the first melt is adjusted towards that of the second melt until the first melt is on the verge of colour instability as hereinbefore defined. 40

3. A method according to claim 2 wherein the oxidation state of the first melt is adjusted towards that of the second melt to a point such that a change of 10 units in the carbon number as hereinbefore defined of the first melt results in a change of transmission of the first melt for a major absorption band of at least 10%. 45

4. A method according to claim 2 or 3 wherein colourant addition or removal is commenced after the first melt has reached the verge of colour instability. 50

5. A method according to any one of the preceding claims wherein the oxidation state of the first melt is adjusted by varying the concentration in the melt of at least one of the oxidizing substances comprising dichromates, arsenic, sodium sulphate, gypsum, barytes and nitre, and, or at least one of the reducing substances comprising slag, aluminium powder, cyanides, carbon, sulphur, calcium sulphide, ferrous sulphide, iron pyrites and iron chromite. 55

6. A method according to any one of the preceding claims wherein the level of the glass melt in the furnace is maintained substantially constant throughout the changeover.

7. A method according to any one of claims 1 to 5 which comprises running out the first melt from the furnace after its oxidation state has been adjusted and filling on the furnace with the second melt. 55

8. A method according to claim 1 substantially as hereinbefore described in any one of the foregoing Examples.

J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square,
Gray's Inn, LONDON WC1 5EU