Scientific Journal of Impact Factor (SJIF): 3.134
ISSN (Online): 2348-4470
ISSN (Print) : 2348-6406

International Journal of Advance Engineering and Research Development

Volume 2, Issue 2, February -2015

INCREASING THE PRACTICAL YIELD OF TBBA - (TETRA BROMO BISPHENOL-A) BY ADOPTING SOME MODIFICATIONS IN THE MANUFACTURING PROCESS TECHNOLOGY

Sorathia Priya D[1] , Dr. Parikh Sachin P.[2], Baldania Ashish D.[3]

[1,2] *V.V.P. Engineering College, Chemical Engineering Department, Virada-Vajdi, Kalawad Road, Rajkot,*
priyasorathia_bechem@yahoo.co.in, sachinparikh@hotmail.com
[3] *Government Engineering College, Chemical Engineering Department, New Rawal wadi, Opposite Ekta Supermarket,*
Sahyog Nagar, Bhuj, ashish2082@yahoo.co.in

Abstract *- The raw materials used for the manufacturing of the TBBA are R.O. water, Bisphenol-A (BPA) MCB, bromine, SMBS, SS and LABSA. This is manufactured by batch process in the industry. The process is initiated with the bromination reaction. The TBBA is used as a raw material for manufacturing of plastic, resins, polymers etc.; as it is flammable retardant material. Moreover it is economically profitable, easy to manufacture, handle and transport. Hence by increasing the yield of TBBA more production of the TBBA is obtained which is beneficial as well as profitable to the industry. This can be done by certain modifications in the process parameters. Thus aim of the paper is to increase the yield of TBBA.*

Keywords: *TBBA, Yield, Distillation, Process Parameters, MCB*

I. INTRODUCTION

A high purity 4,4'-isopropylidine-bis-(2,6-dibromophenol) characterized by ionic bromides less than 10 ppm, colour in alkaline solution from 60-100 HU, HPLC purity about 99.9%, APHA of 20% MeOH solution less than 10.0 HU, Fe less than 1.0 ppm, turbidity of 20% MeOH solution less than 5 NTU, pH of 10% slurry 6.0-7.0, size of the crystal particles, 250 to 280 microns with angle of repose lower than 30°. The product is produced by reacting Bisphenol-A with bromine in a "water-immiscible" polar solvent in the presence of hydrogen peroxide, aging the reaction products after the reaction, eliminating the excess bromine by reducing agents, washing the product layer with a combination of anionic surfactant, alkali, reducing agent and demineralised water under controlled pH conditions, partially distilling the organic solvent chilling

the medium containing the product, filtering the crude product, boiling the crude product with alkali, reducing agent and demineralised water, filtering the TBBA, washing the product with demineralised water and drying to obtain the final high purity TBBA with high yield. Uses two phase solvent systems consisting of 0.2-20 parts of water and one volume of unreactive "water-immiscible" liquid organic solvent such as CH2Cl2. The bromination is carried out under reflux conditions for 6 hours with gradual separation of TBBA the isolated TBBA has melting print 181-3 degree C. This process has severed problems related to recovery of HBr for re-use resulting in losses of expensive raw material.

Attempts to overcome the weaknesses in the re-use of HBr by introducing an aqueous solution of hydrogen peroxide in the reaction medium. Several other oxidizing agents such as chorine, bromine for insitu conversion of HBr to Br2 in the reaction medium have been suggested. However, this suffered from problems of low yield (75-95%) of the crude product which included the di, tri and tetra brominated products. Repeated use of to mother liquor cold enhances the yields but make the process cumbersome and unsuitable for manufacture scale operations. Addresses the problem of separation of the brominated product from the emulsion obtained at the end of the reaction with the addition of above 100 ppm of a surface active agent. The yields continued to be in the range of 89.3% to 95.2% with unsatisfactory product quality. Another Japanese Patent 79119452 (1978) attempted the purification of TBBA by dissolving it in aqueous sodium hydroxide followed by addition of hydrochloric acid to reprecipitate the product. However, the end product suffered from color problems, as the APHA (color) of the end product did not go below 30.Described a process of manufacture of TBBA in which the reaction of bisphenol A with bromine is carried out in the presence of a substantially "water-immiscible" organic solvent constituent and an aqueous constituent comprising hydrogen peroxide and by incorporating not more than 100 ppm of a surface active agent. The mother liquor resulting from the separation of the TBBA product is recycled to the reaction system. The final product was of 99.5% (by gas chromatography) and yield of 95%. This patent has however not commented on the colour characteristics (APHA) of the end product and the level of ionic impurities, which are critical in deciding on its end application.

Outlines a substantial improvement on earlier processes which involves bromination of Bisphenol A in inert solvents, in the presence of hydrogen peroxide acidified with mineral acids (in quantities less than required to convert all, HBr formed to Br2). On completion of the reaction the reaction mass is boiled and the aqueous and non-aqueous phases are allowed to separate. The HBr co-product (with TBBA) in the non-aqueous phase is separate, washed with aqueous alkali sulphite solution and rinsed with deionised water. The final product is heat treated from 30 seconds to 1 hour. The end product is claimed to have <20 ppm ionic impurities. However this patent has claimed high yield "without disclosing" quantitative yield figures. The quality in terms of the colour (APHA) or texture of the end product has also not been disclosed. The emphasis of the U.S. patent is on reduction of ionic impurities by the extra heating process of the end product. Disclosed attempts to crystallize TBBA using alcohol to get large particle size single crystals ranging from 150-500 microns. However the process described are fraught with practical difficulties for industrial production. The TBBA obtained by the process have an angle of repose in the range 35° to 45°. Importantly, solvent used in such process is an alcohol solvent, which can lead to the production of undesired by-products. Also in such process, it is found to be extremely difficult and tedious to recover the solvent form the aqueous stream and involves complex recrystallation from an alcohol solvent. The process is further cost extensive as the same involves use of costly hydrazine hydrate for killing of bromine. It is also known from prior dated U.S. Pat. No. 5,068,463 which corresponds to EP 0424895A of yet another process for the production of TBBA which suggest the washing of the organic phase containing dissolved tetrabromo-4,4-alkylidendephenol with an aqueous alkali sulphite solution preferably at 50-90° C. While this process outlines manufacture of TBBA of high purity, the product obtained is found to have APHA in the range of 10 to 70 HU. Also, the process involves the use of sulfuric add for bromination and washing is found to be not effective in removal of undesired iron content from the product.

Thus while several processes for manufacture of TBBA have been made available and known to the art over the years, it has not yet been possible to obtain the same having HPLC purity of 99.9% ionic bromide less than 10 ppm, angle of repose tae than 35° and alkaline APHA less than 100 HU. Also, particle size of such product of the known art is found to have limitation i.e. in the range of up to 250 μm only. Also the process for the manufacture of TBBA presently available in the art as discussed above we found to be complex and presently available in the art as discussed above are found to be complex and also cost-extensive. Thus for the above reasons, the industrial demand for processing with high yield and high purity TBBA still continues. It is thus the basic object of the present invention to provide TBBA of high purity having HPLC purity of 99.996 ionic bromides less than 10 ppm, angle of repose less than 35° and alkaline APHA less than 100 HU. Another object is directed to a process of manufacture of TBBA of high purity as above with particle size ranging from 250 to 280 microns. Another object of the present invention is to provide for a process for manufacture of TBBA of high purity which would enable obtaining TBBA of the above said purity and characteristics. Another object of the present invention is directed to the process for manufacture of TBBA which would result in TBBA of high purity and characteristics as above and at the same time would be simple and cost effective

A further object is directed to manufacture of TBBA using solvent which can be readily recovered and recycled to make the process cost effective. Yet further object is directed to provide a process for manufacture of TBBA of high purity with yield of over 95%.

II. MATERIALS & METHODS

The process in the present invention involves the following steps; charging Bisphenol-A to water-immiscible "non-polor" and water; feeding hydrogen peroxide in this mixture; adding appropriate quantity of Bromine to the reaction mixture at a specified range of temperatures and time sufficient of tetrabrominate the BisphenolA;aging the reaction mixture; destroying the excess bromine at the end of the reaction using Sodium Meta-bi-sulphite; washing the product (non-aqueous phase) with a combination of anionic surfactant alkali, sodium meta-bi-sulphite and demineralised water; distilling out major part of the solvent; chilling the concentrated product layer and then filtering the crude product; boiling the crude product with water, sodium meta-bi-sulphite and alkali;filtering the product and washing the cake with demineralised water; drying the product. The solvent used in the present invention may be selected from a wide range of non-polar solvents which have low solubility in water and these selected should demonstrate easy and speedy phase separation. Halogenated hydrocarbons halogenated aromatics and aromatics, chlorobenzene or ethylene dichloride are preferred. 5-10 moles of the solvent per mole of Bisphenol A is suitable. The strength of Hydrogen Peroxide may vary from 10-50% w/w. Although in principle any surface-active agent can be used to ease the phase separation between the organic and aqueous layer, anionic surfactants are most suitable for enhanced phase separation and solvent recovery. 35-100 ppm of surfactant per mole of Bisphenol-A is adequate for the required purpose. The inventors have surprisingly found that washing the organic layer containing the product TBBA and co-product Br is best washed by a combination of demineralised water, alkali and sodium meta bi-sulphite at 75-90° C.

Maintaining pH from 2-4 during the washing stages. The alkali used may be alkali metal hydroxides, carbonates or their combinations. The washed organic layer containing TBBA may be chilled at 5-10° C. to obtain the crystals of TBBA. However, when 70-80% of the solvent in the organic layer is distilled and the concentrated organic layer is chilled the yield of crude TBBA is considerably increased. The entrapped or embedded ionic bromide in TBBA crystals varies from 30-40 PPM. Another significant finding of the present invention is the process of obtaining TBBA of very high purity. When the crude TBBA (continuing 30-40 PPM ionic bromide) is boiled with demineralised water, sodium meta bi-sulphite and alkali at a pH 5.5-6.0 and further washing of the recovered TBBA with demineralised water followed by normal drying at 70° C., a final product with ionic impurity <10 PPM is obtained. No heating at high temperatures or washing with surfactants etc. is necessary. The treatment in the present invention also ensures a product with high yield of good colour and textural characteristics. The process of the invention is being illustrated by non-limiting examples.

- **Operational Procedure Of TBBA**

1. Charge 900 kg DM Water.
2. Start Agitator.
3. Charge 1500 kg Bisphenol-A (BPA)
4. Start chilled brine/Water circulated in the jacket.
5. Close manhole and charge 3624 kg fresh/recovered MCB
6. Send sample H_2O_2 to QC to check purity 50% and specific gravity 1.18.
7. Charge 1030 kg H_2O_2 as above specification or as per purity of H_2O_2.
8. After achieving temperature between 20 ˚C to 30 ˚C and start Bromination.
9. Charge Bromine 2160 kg.
10. Maintained temperature between (20 ˚C to 30 ˚C) during Bromination.
11. At the end of Bromination, stop chilled brine/chilled water circulation and increase the temperature to (48 ˚C to 52 ˚C) by Bromine addition.
12. Maintained the temperature to 48˚C to 52˚C for 2 hours.
13. Draw a sample from reactor and check the purity and melting point.
14. If purity of reaction mass is less than 99% and melting point is less than 180 ˚C then maintained the reaction mass for 1 hour and again take the sample.
15. If purity of reaction mass is more than 99% and melting point is more than 180 ˚C then charge 123 kg SMBS in 904 lit water in reaction mass and stirred for 30 minute.
16. Add catalyst 0.09 kg LABSA in 10 lit water and stirred reaction mass for 15 min and settle for 15 min.
17. Separate the upper aqueous layer by siphoning.
18. Start stirring and charge SMBS solution (25 kg SMBS in 100 lit DMW) into the reaction mass.
19. Raise the temperature to 82 ˚C to 85 ˚C and maintained temperature for 30 min.
20. Charge 3000 kg DM Water into reaction mass and maintained reaction mass for 30 min at 82 ˚C to 85 ˚C.
21. Settle the reaction mass for 15 min and separate the upper aqueous layer by siphoning.
22. Charge 1500kg DM water in reaction mass and adjusts pH to 6.5 to 7.0 by SS solution (123 kg SS + 1890 lit DMW)
23. Raise the temperature and distilled out 70% MCB.
24. Start cooling water circulation and cool the reaction mass to 45 ˚C
25. Chilled the reaction mass to 18 ˚C to 20 ˚C by chilled water circulation.
26. Maintained the temperature at 18˚C to 20˚C at 1 hour.
27. Filter the cake in agitated nutch filter.
28. Give three DM Water wash (2500 lit per wash) in agitated nutch filter and suck dry the wet cake.
29. Unload the wet cake in tube box and shift near vessel for repulpling.
30. Charge 5300 lit DM water into the reactor and wet cake unloaded from agitated nutch filter.
31. Adjust pH 6.5 to 7.0 by SS solution (5 to 10 lit 20% w/w DMW) and stirred for 15 min.
32. Raise temperature to 95˚C and collect MCB by isotropic distillation and maintained 99 ˚C temperature 1 hour after distillation.
33. Start cooling water circulation and cool the reaction mass to 65 ˚C to 70˚C.
34. Filter the cake in agitated nutch filter.
35. Give three DM Water washes (2000 lit + 2000 lit +2500 lit) in agitated nutch filter and dry the wet cake.
36. Unload the wet cake in hopper and fed to spray dryer for drying.
37. Dry the material at 80 ˚C to 90 ˚C.
38. Pulverize the product in pulverizer and pack in jumbo bags/High Density Poly Ethylene (HDPE) bags as per requirements.

- **Process Description**

In the reaction Bisphenol-A (BPA) is reacted with bromine in the presence of MonoChloroBenzene (MCB) as a solvent, Hydrogen peroxide as a oxidizing agent and water (DMW). In the reaction Bromine in slightly excess added to stirred Bisphenol-A solution in MonoChloroBenzene in a suitable reactor at 25 to 30 °C, the exothermic reaction is controlled by the rate of bromine addition. After bromination to kill the free Bromine in the reaction mass by a Sodium Meta Bisulphate (SMBS) and neutralize the reaction mass by Sodium Sulphate (SS). In solvent recovery section reaction mass after Bromination, neutralization and washing taken in distillation vessel at 82 to 97°C temperature and recover 70% Monochlorobenzene (MCB).In the product recovery section product solution cooled to crystallize the product TBBA after distillation of MCB. Crystallize TBBA product is recovered by filtration incorporating a water wash stge. The residual MonoChloroBenzene in the filter cake is removed by repulpling operation.

1. To increase the recovery of MCB from 70% to 72% at first experiment, reaction mass of batch is done at lab scale by using electric heater.
2. In first stage 72% recovery is obtained. Calculate the yield of TBBA.
3. In second stage 72 to 74% recovery is obtained. Calculate the yield of the batch and check the parameter of product quality.
4. In second stage the mass recovery is 74%, yield is increased but it affects the product quality. So, for MCB solvent recovery is to be carried out between 73- 74%. Take 73.4% of solvent recovery to increase the yield of TBBA.
5. At 73.4% of MCB recovery as compared to 70% the yield of the batch is increased from 3.15 to 3.30kg and no adverse effect in product quality of batch.
6. Result : improve the yield from 3.15 to 3.30

III. RESULTS & DISCUSSION

1. Thus the present invention relates to 4,4'-isopropylidene-bis-(2,6-dibromophenol)characterized by ionic bromides less than 10 ppm, colour in alkaline solution from 60-100 HU, HLPC purity about 99,99%, APHA of 20%.

2. MeOH solution less than 10.0 HU; Fe less than 1.0 ppm, turbidity of 20% MeOH solution less than 5.0 NTU, pH of 10% slurry 6.0-7.0 average particle size of 250-280 microns and angle of repose equal to or less than 35°.

3. The present invention also relates to a process for preparation for high purity 4,4'-isopropylidine-bis-(2,6-dibromophenol) comprising a reaction of Bisphenol-A with bromine in a "water-immiscible" polar solvent in the presence of hydrogen peroxide, aging the reaction products after the reaction, eliminating the excess bromine by reducing agents, washing the product layer with a Combination of anionic surfactant, alkali, reducing agent and demineralised water under controlled pH conditions, partially distilling the organic solvent chilling the medium containing the product, filtering the crude product, boiling the crude product with alkali, reducing agent and demineralised water, filtering the TBBA, washing the product with demineralised water and drying to obtain the final high purity TBBA with high yield.

4. By the process there is obtained of free flowing TBBA in yields (~96.5%) and purities (99,9% by HPLC) mp 183° C. ionic bromides<10 ppm, colour or 20% alkaline solution<100 HU, with particle size 250-280 microns most suitable for the wide range of industrial applications.

IV. CONCLUSION

Yield is increased from 3.15 to 3.30 on lab scale. Due to this production is increased & profit is obtained, losses of MCB are reduced as 70% to 73.4% of MCB is recovered. As per Material Safety Data Sheet of Tetra Bromo Bisphenol-A and MonoChloroBenzene the solubility of TBBA in water is 1.25mg per 1 litter of water and in MCB is 0.14kg per 1kg of MCB, MCB charging per batch is 4049kg.

REFERENCES

1. Lowe, Cerrito, Durkee, El Sorbate And Claif (1971) Us Patent No.-Us3552574.
2. Frank Lawson, (2001) Us Patent No.-Us6693139b2, Page No.-1.
3. Gregory W. Bachman, Robert S. Loken, Julie G Sterling and Thomas K Mallmama. (1999) Us Patent No.-Us6693139b2.
4. William Harold .(1998) Us Patent No.-Us7001523b1, Page No.-1
5. Hirosh. (2001) Us Patent No.-Us48636081, P.No.-1