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(71) Applicant: **ALBEMARLE CORPORATION** [US/US]; 451 Florida Street, Baton Rouge, LA 70801-1765 (US).

(72) Inventors: **SHOFNER, Justin, P.**; 7225 Sheffield Court, Baton Rouge, LA 70806 (US). **OURS, Evan, A.**; 4000 Lake Beau Pre Boulevard, #75, Baton Rouge, LA 70820 (US).

(74) Agents: **HOEFLING, Marcy, M.** et al.; ALBEMARLE CORPORATION, Law Department, 451 Florida Street, Baton Rouge, LA 70801-1763 (US).

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(54) Title: METHOD FOR PREVENTING THE FORMATION OF EMULSIONS ASSOCIATED WITH BROMINATION OF POLYSTYRENE

(57) Abstract: Provided is a method for suppressing the formation of emulsions encountered in the quenching of polystyrene bromination reactions with aqueous quenching agents. The method comprises the exposure of the polystyrene bromination substrate to molecular sieves in a halogenated alkane solvent prior to bromination.

METHOD FOR PREVENTING THE FORMATION OF EMULSIONS ASSOCIATED WITH BROMINATION OF POLYSTYRENE

BACKGROUND

[0001] In the practice of preparing polystyrene polymers, particularly halogenated polystyrene polymers such as those used in fire-retardant applications, halogenation agents such as bromine, chlorine, fluorine, and the like, are often used. In the case of bromine, such reactions yield hydrogen bromide as a side product of the halogenation reaction. Bromination is generally carried out in organic solvents such as alkanes, halogenated alkanes, aromatics, and the like.

[0002] Polystyrene polymers generally contain multiple bromination sites, and it may not be desirable to brominate them all. While the degree of bromination can be controlled by selecting the proportions of bromination reagent to bromination substrate, it is more efficient to use a small excess of bromination reagent relative to the desired proportion of sites which are to be brominated. In that the bromination reaction must be carried out such that only the desired degree of bromination can be achieved, it can be necessary to terminate bromination prior to completion. The bromination reaction can be terminated by the use of quenching reagents such as, for example, hydrazine hydrate or sodium hydroxide. The quenching agent generally stops the bromination reaction by reacting with bromine present in the solution. Once the bromination reaction has proceeded to the desired degree, quenching is generally carried out by combining the reaction mass with aqueous solution of the quenching agent. For example, the reaction mass can be added to a hydrazine hydrate/water solution. One advantage of using an aqueous quenching agent is that many products of the quenching reaction (such as, for example, hydrogen bromide in the case of a hydrazine hydrate quench) are sequestered in the aqueous phase, with organic products, if any, remaining in the organic layer which contains the brominated polystyrene polymer, as well as solvents in which the bromination reaction was taking place. Common bromination solvents include alkanes, halogenated alkanes, aromatics, halogenated aromatics, and the like.

[0003] Please note that even when brominating fully, the bromination reactions do not reach full completion due to the asymptotic nature of the reaction, and bromine is thus often used in great excess. Thus, residual bromine is generally present, often in significant amounts. While such a situation differs from the above-described reaction in that the

bromination terminates due to a lack of bromination substrate, the "quenching" step is still necessary in order to convert excess bromine to hydrogen bromide, allowing for safe handling of the reaction mass and further processing of the halogenated polystyrene product.

[0004] The quenching step generally results in a two-phase mixture consisting of an emulsified organic layer containing an amount of entrained aqueous phase, on top of which resides an aqueous phase comprising excess aqueous which was not entrained in the organic emulsion. The organic component of the emulsion comprises brominated polystyrene as well as the solvent in which the polystyrene was brominated. The aqueous phase consists of water and the quench step products, such as, for example, hydrogen bromide in the case of a hydrazine hydrate quench. In general, as much as or more than 40 wt % of the total aqueous phase can be entrained within the organic phase emulsion. The reaction products of the quench step are generally undesirable and must be removed because, among other things, they can have adverse effects on many end-user applications such as electronics. In some cases, such as with a hydrazine hydrate quench, the reaction products must be further processed (hydrogen bromide is neutralized with a caustic, such as sodium hydroxide) which introduces further ionic species (such as sodium bromide) into the reaction mixture.

[0005] Because of this, they are removed before further isolation and processing of the product. However, the removal is complicated by the fact that water soluble species, such as for example ionic species, are part of the aqueous phase, much of which sequestered away within the polymer emulsion in the organic product phase. A common method purifying the polymer product phase is to wash with water to attempt to extract ionics and/or any other water soluble products. However, the efficiency of such washes can be greatly reduced if emulsions are present because much of the aqueous phase is entrained within the polystyrene product phase, making it difficult to extract. Any neutralization steps generally require large amounts of caustic and repeated exposures in order to sufficiently neutralize the hydrogen bromide retained within the emulsified aqueous phase. Any other bromination or quenching reaction side products which are soluble within the aqueous phase are also trapped in the emulsion as a part of the entrained aqueous phase.

[0006] Emulsion formation upon quenching is generally difficult to avoid with brominated polystyrene reactions, regardless of the molecular weight of the polystyrene, especially without adding other components to the polystyrene solution which must be removed later in order to preserve product quality. However, despite the foregoing, it has

heretofore been thought that water soluble contaminants, such as acid and/or ionic content, must be addressed through repeating washing by extraction with water downstream of the quenching reaction.

BRIEF DESCRIPTION OF THE INVENTION

[0007] Because of the impurities present in the aqueous phase, the emulsification of the halogenated polystyrene polymer reaction mass inevitably increases the complexity and extent of purification procedures in the downstream processing of the polystyrene. However, it has been found that the emulsion formation can be suppressed or even prevented by contacting the bromination substrate with specific molecular sieves prior to bromination, removing the sieves, and proceeding with the bromination. It has been found that the emulsion suppression is most pronounced if the contacting takes place in a halogenated alkane solvent. The fact that the suppression is particularly effective when the contacting takes place in a halogenated solvent is convenient because many methods of preparing the polystyrene bromination substrate give solutions of polystyrene solvated in halogenated alkane solvents. Thus in one embodiment, the present invention comprises: A method for preventing the formation of a polystyrene emulsion, said method comprising the following steps:

1) providing a solution comprising polystyrene substrate which is dissolved in a halogenated alkane solvent or dissolving a polystyrene substrate in halogenated alkane solvent to form a dissolved polystyrene substrate solution;

2) contacting the dissolved polystyrene substrate solution of 1) with one or more molecular sieves;

3) separating the one or more molecular sieves from the dissolved polystyrene substrate solution such that the dissolved polystyrene substrate remains dissolved in the halogenated alkane solvent;

4) following the separation of step 3), contacting the dissolved polystyrene substrate solution with a bromination agent; wherein the contacting optionally occurs in the presence of a catalyst, such that the dissolved polystyrene substrate is brominated through a bromination reaction; and

5) contacting the brominated polystyrene substrate solution with an aqueous quenching reagent, thereby quenching the bromination reaction.

[0008] It has also been found that after exposure to the sieves and prior to bromination, the polystyrene substrate can be separated from the sieves and resolvated in the same or another halogenated alkane solvent and the effects of sieve exposure are retained, i.e., the formation of an emulsion is suppressed.

[0009] In a preferred embodiment the sieves have an average pore size in the range of from about 2 to about 12 Angstroms. In another preferred embodiment, the contacting takes place for a time in the range of from 1 to 12 hours. In another preferred embodiment, the sieves are present at a loading of 0.5 to 5.0 wt% mol sieves relative to polystyrene. In another preferred embodiment, the sieves are present at a loading of 0.5 to 2.0 wt% mol sieves relative to polystyrene.

[0010] In another embodiment, the present invention comprises a polystyrene polymer dissolved in a halogenated alkane solvent which has been exposed to molecular sieves according to the method set forth above, the sieves having been removed. In yet another embodiment, the present invention comprises an solution of halogenated polymer, wherein the polymer solution has been formed by steps 1-5 above.

[0011] The present invention is directed at decreasing the incidence of water soluble contaminants associated with brominated polystyrene polymers as a result of bromination, quenching and/or further steps, such as, for example, neutralization of quenching products, which result in water-soluble contaminants emulsified as part of an aqueous phase with the brominated product polymer. In one embodiment the contaminants are ionic species formed by the neutralization of an acid in an organic phase with an aqueous base.

[0012] Such a situation can arise when a bromination reaction is quenched with a reagent which yields an acidic species as a quenching product, which is subsequently partially or fully neutralized by the addition of a neutralizer. For example, bromination with bromine can be quenched by the addition of hydrazine hydrate, giving hydrogen bromide as a quenching product. The hydrogen bromide is neutralized by the further addition of a base such as, for example, sodium hydroxide.

[0013] Alternatively, the bromination can be carried out such that the quenching reaction gives products which are not further processed. For example the bromination of polystyrene with bromine can be quenched by the addition of sodium hydroxide, giving NaBr which is generally not further treated prior to removal.

[0014] The present method, which gives an organic phase in which the emulsification is less than with methods having no sieve exposure, and in many instances, even completely absent. The reduction in degree of emulsion, or elimination of emulsion altogether

simplifies further processing of the polymer in the organic phase. The HBr produced during bromination and present in the aqueous phase upon quenching, as well as other water-soluble contaminants which may be produced by the quenching reaction or further post-quenching processing, such as neutralization, are accessible to being completely or largely removed by washing steps, rather than being entrained in an emulsion within the organic phase. The removal of the water soluble contaminants and ionics in an initial washing step decreases the need for further washing. In the case of further processing by neutralization, it allows the hydrogen bromide thus produced to be cleanly neutralized with a minimum of caustic. Overall, the exposure of the polystyrene substrate to sieves in a halogenated solvent reduces the amount of water soluble contaminants and ionics which would end up as brominated polystyrene product contamination.

[0015] Furthermore, the separation is often quick and visually clean, which enables the easy efficient and complete removal of the aqueous phase and associated solvated or dissolved impurities. As mentioned above, if a neutralization is to be carried out, the effective partitioning of the hydrogen bromide into the aqueous phase leads to lower material cost due to the decreased amount of caustic required for neutralization. Furthermore, cycle times are decreased due to quicker phase separation and fewer wash steps. Throughput is increased due to the decreased amount of aqueous required and the shorter batch time. Decreased product ionic content leads to higher product quality. Overall improvements in process time and product quality are generally expected to result in significant cost savings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Fig. 1 depicts a separation funnel containing a bromination reaction work up as prepared in Example 1, having no exposure to molecular sieves. The reaction work-up includes an emulsified organic phase containing brominated polystyrene, bromochloromethane solvent, and an entrained aqueous phase which in itself contains hydrogen bromide, other ionics, and other impurities (milky lower layer). The funnel also contains a residual aqueous phase (upper layer) which contains the same components as the entrained aqueous phase.

[0017] Fig. 2 depicts a separation funnel containing a bromination reaction work up as prepared in Example 2, which has been exposed to molecular sieves for approximately 12 hours prior to bromination. The funnel contains a clear aqueous layer (upper layer) consisting of undesirable components such as hydrogen bromide, other ionics and

impurities, and a clear organic layer (with no emulsion) containing brominated polystyrene and bromochloromethane solvent.

DETAILED DESCRIPTION

[0018] As noted above, the fact that halogenated alkanes are preferred solvents in which to expose the polystyrene bromination substrate is particularly convenient because some methods of preparing polystyrene polymers give a solution comprising polystyrene which is dissolved in a halogenated alkane solvent. In one embodiment, the polystyrene bromination substrate is prepared according to the methods disclosed in copending applications US 20110178226 A1 and US 20110130520 A1, the disclosures of which are hereby incorporated by reference.

[0019] The formation of emulsions upon the quenching of bromination has been observed with polystyrenes of a wide range of M_n and M_w values. For instance emulsion formation has been observed with polystyrene polymers having M_n values as low as 500 or even lower, and M_w values as low as 650 or lower. On the other hand, emulsion formation has also plagued the bromination of polymers having M_n values as high as 125,000 Daltons or even higher and M_w values as high as 210,000 Daltons or even higher. Without desiring to be bound by theory, it is thought that the emulsion suppressing effect of the sieves could be due to an emulsion stabilizing component which is removed or changed upon contact with the sieves. Thus, the applicability of the inventive method should be wide, and relatively independent of polymer size. The polystyrene used in the process of the present invention generally includes polystyrene having M_n and M_w values up to and including 200,000 Daltons, and 300,000 Daltons respectively. In other embodiments, the polystyrene used in the present inventive process is characterized by M_n values above 500 Daltons and M_w values above 650 Daltons. In still other embodiments, the polystyrene used in the present inventive process is characterized by M_n values in the range of about 500 to about 600 Daltons, and M_w values in the range of about 650 to about 750 Daltons. In still other embodiments, the M_n values are in the range of about 90,000 to about 125,000 Daltons and the Mw values are in the range of about 170,000 to about 210,000 Daltons. M_n and M_w have meanings as understood in the art. In general, the inventive method is expected to be applicable to polystyrene polymers of all sizes which form emulsions upon quenching of the bromination reaction with aqueous quenching reagent.

[0020] The molecular sieves which can be used in the present invention include those having average pore sizes in the range of from about 2 to about 12 angstroms. More preferred are average pore sizes in the range of from about 2 to about 6 angstroms. Most preferred are zeolite molecular sieves having average pore sizes in the range of from about 3 to about 5 angstroms, such as 4A molecular sieves. In a preferred embodiment, the polystyrene bromination substrate is prepared according to the methods disclosed in copending applications US 20110178226 A1 and US 20110130520 A1, the disclosures of which are hereby incorporated by reference. Such methods give a polystyrene bromination substrate with M_n and M_w values which can be treated by the process disclosed herein. However, it should be noted that emulsion formation is a common problem experienced in the formation of polystyrene, regardless of the M_n and M_w values of the polymer being prepared, and the exposure to molecular sieves is expected to have at least some degree of emulsion-suppressing ability with polystyrene polymers having a wide range of M_n and M_w values.

[0021] In a preferred embodiment, the polystyrene mass is exposed to the molecular sieves prior to the bromination reaction. It is preferred that the polystyrene in an organic solvent which comprises one or more monohalogenated or multihalogenated alkanes or alkenes, with halogenated alkanes of six carbons or less, such as bromochloromethane, being preferred. Surprisingly, it has been found that the use of toluene as the solvent in which the polystyrene substrate is exposed to the sieves does not result in emulsion-breaking exhibited by halogenated alkanes, such as bromochloromethane.

[0022] The exposure can be carried out by simply adding the sieves to the substrate dissolved in the foregoing solvent. In one embodiment, the sieves are held relatively stationary in a column, such that the dissolved polystyrene substrate is flowed through the column such that it contacts the sieves as it flows past them.

[0023] The exposure to molecular sieves is generally for times on the order of about 6 hours, although times as short as 1 hour, or even shorter are expected to give some degree of beneficial result, such as partial suppression of the emulsion with respect to unexposed substrate. Preferred exposure times are times as long as at least about 4 hours, with times as long as 6 hours being more preferred. While longer times generally give, to a degree, more complete emulsion suppression, times longer than 12 hours are generally expected to give the maximum emulsion suppression.

[0024] The molecular sieve loading, i.e, the amount of sieves as a ratio to the amount of polystyrene, can be in the range of from about 0.5 wt% and 5.0 wt%, or more preferably

0.5 wt% and 2.0 wt%, or even lower or higher than this range. A sieve loading in the range of from about 0.7 wt% to about 1.5 wt% is preferred.

[0025] In general, it has been observed that a wide variety of polystyrene substrates (i.e., substrates having a wide variety of M_n and M_w values) are subject to the formation of emulsion upon aqueous quenching. Also, emulsion susceptibility can exhibit a degree of dependence upon the source or method of preparation of the substrate. However, the exposure to molecular sieves prior to the bromination step as described herein has resulted in reduced or absent emulsion formation with respect to substrates which have not been exposed. It may thus be necessary to perform a test in order to determine the amount necessary to partially or fully suppress emulsion formation. In general, it should be expected that the amount of sieve loading which is effective at suppressing emulsion formation increases with the propensity of a given substrate to form emulsions upon quenching. Furthermore, while increasing the sieve loading can be expected to reduce the propensity to form emulsions, the effect is expected to reach its maximum at some sieve loading value (in many or even most cases, the effect can be complete suppression), above which, no further suppression is seen. In some cases the sieve loading value may be 3, 4 or even 5 wt%. In other cases, a sieve loading of 0.5 wt% may have no little or no effect, with larger sieve loadings required in order to observe significant suppression. However, in general, the ambit of the present invention includes the use of sieves to partially or fully prevent the formation of emulsions normally seen upon the introduction of aqueous media to a polystyrene bromination reaction taking place in a halogenated alkane solvent.

[0026] Following sieve exposure, the sieves are separated from the polystyrene substrate. The separation can be such that the sieves are removed from the substrate and solvent. The sieves are generally filtered out after exposure by means such as mechanical separation means. However, separation of the sieves from the reaction mixture can be performed by the use of other separation methods, such as gravimetric or centrifugal methods. In other embodiments, the polystyrene substrate is separated from the solvent and sieves.

[0027] The substrate is then brominated in an organic solvent. In one embodiment, the bromination reaction is conducted in the same solvent or mixture of solvents in which the unbrominated polymer is exposed to the molecular sieves. In other embodiments, the reaction mixture containing the polystyrene bromination substrate and bromination agent can be formed by adding the brominating agent, neat or in a solvent, to a the bromination substrate and organic solvent. Bromine is the preferred bromination agent. In a

convenient, embodiment, the reaction mixture in which the bromination takes place is created by separately co-feeding bromine and the sieve-exposed substrate to a solution of bromochloromethane and a bromination catalyst. If desired, the bromine can be dissolved in a solvent, such as a halogenated alkane, such as BCM, such that the bromine is co-fed along with a substrate/BCM solution to a waiting mass of solvent and catalyst. It is preferred to agitate during the entire period of addition. The reaction mass is kept at a low temperature, such as, for example, 0°C, for the duration of the time that the materials are fed. Convenient bromination catalysts include aluminum chloride ($AlCl_3$), aluminum bromide ($AlBr_3$), but other bromination catalysts can be used. For a full bromination, a bromine to polystyrene mass ratio of roughly 5.5 can be used.

[0028] The reaction mixture containing the polystyrene mass which is being brominated is then quenched by the addition of a quenching agent such as hydrazine hydrate or sodium hydroxide, added as an aqueous solution, reacting with remaining bromine to form hydrogen bromide. In general, it is preferable to add the quenching reagent in amounts such that an excess exists relative to the stoichiometric ratio of the quenching agent and the bromine (in the case of hydrazine hydrate, 1 mole hydrazine to 2 moles bromine).

[0029] The present process can be used on halogenated polystyrene masses which form emulsions upon the quenching of the halogenation reaction with aqueous quenching reagents. Reagents for quenching the bromination reaction include sodium hydroxide, sodium sulfite, hydrazine hydrate, and the like. Bromination solvents can include one or more of the following: dibromomethane, dichloromethane, bromochloromethane, chloromethane, bromomethane, bromochloromethane, and the like. In the preferred embodiment, the polystyrene can be polystyrene substrate which is prepared according to the method in copending applications US 20110178226 A1 and US 20110130520 A1.

[0030] The polystyrene polymers which can benefit from the process of the present invention include halogenated polystyrene polymers which are halogenated in an organic phase, followed by further treatment which introduces an aqueous phase, such as for example, quenching with an aqueous reagent, which results in the formation of a polystyrene polymer emulsion in the organic phase.

[0031] The emulsion can be such that the entire aqueous phase component is included in the emulsified organic phase. Alternatively, the emulsion can be to such an extent that the polystyrene mass is completely emulsified with some of the aqueous phase but aqueous phase which is not part of the emulsion is also present as a separate top layer.

[0032] The use of molecular sieves has been shown to lessen the complications arising from the brominated polystyrene product having a high ionic content.

[0033] The wash efficiency (WE) parameter is a measure of the relative amount of emulsion-retained aqueous phase after the quenching step has been performed. It is thus a measure of the ability of sieve exposure to suppress emulsion formation. In a broad aspect, the WE is the ratio of 1) the weight of the aqueous phase used to quench the bromination to 2) the weight of the unemulsified aqueous phase after quenching. The latter can be determined by performing a phase separation to yield an emulsified phase and an aqueous phase, and weighing the separated aqueous phase.

[0034] Theoretically, the wash efficiency can simply be measured upon performing the above phase separation. However, in practice, the interface between an emulsified phase and an aqueous phase can be difficult to distinguish, which can, in some instances, lead to significant errors in the WE calculation. For instance, the organic phase weighs considerably more than the aqueous phase (the density (i.e., weight per volume) can be twice as much as that of the aqueous phase), and it is common to use a quench volume which is about one third that of the aqueous phase. In such a situation, the mass ratio of the organic phase to the aqueous phase is about six. If the separated aqueous phase includes even a small amount of organic phase, the wash efficiency can be significantly affected if it is calculated by simply separating and weighing.

[0035] However, water soluble species which are present in the aqueous phase partition with the water, and their relative amounts can also be used to determine WE. For example, hydrogen bromide is present in the organic phase as a result of bromination, and upon quenching, it becomes solvated in the aqueous phase. It can be convenient and accurate to measure the wash efficiency by measuring the amount of hydrogen bromide in the aqueous phase. This can be done by the following simple, accurate procedure:

1) Quench with a measured volume of quenching reagent.

2) Separate the aqueous phase from the emulsion phase. If an interphase transition layer is present, include it with the aqueous phase.

3) Measure the concentration of hydrogen bromide in the separated aqueous phase, such as, for example, by removing an aliquot of pure aqueous phase and performing the measurement titrimetrically.

4) With the emulsion phase, perform an extraction by adding water in the same measured amount as in step 1.

5) Measure the hydrogen bromide concentration in the aqueous phase produced in step 4).
6) Calculate the WE by taking the ratio of the hydrogen bromide concentration of step 3) with that of step 5).

[0036] The wash efficiency is defined as the ratio of the wt of the HBr in the aqueous phase after quenching to the wt of the HBr in the aqueous phase after washing. It essentially measures the degree of HBr extraction into the aqueous layer introduced with the quench step.

[0037] In general, a high wash efficiency, as defined, corresponds to a low degree of emulsion formation, as it indicates that following the quenching step, a large amount of aqueous phase is not bound up in an emulsion and can thus be washed away. A low wash efficiency, in contrast, means that a relatively high amount of water and water insoluble species from the quench are entrained in the organic phase as an emulsion.

[0038] Other water soluble species can be present in the aqueous layer, such as from bromination or quenching, and the above method can be applied to other water soluble species as well in order to get a WE value. However, the measurement of hydrogen bromide is likely to be the most accurate as hydrogen bromide is produced in large amounts during bromination. However, the measurement of the concentrations of other species, such as for example, sodium (such as would be present upon quenching with sodium hydroxide) can also be used to determine WE.

[0039] Using the method of the present invention, wash efficiencies as high as 200 can be obtained, with wash efficiencies in the range of from about 20 to about 100 being more common.

[0040] It should be noted that in some cases the emulsion formation is suppressed such that one of ordinary vision would not be able to visibly detect the formation of any degree of emulsion, such as translucent or opaque formations, after quenching with aqueous quenching agent.

EXAMPLES

Example 1

Observation of emulsion formation in polystyrene polymers formed on a laboratory scale

[0041] Unbrominated polystyrene substrate, having M_n in the range of 500 to 600 Daltons and M_w in the range of 650 to 750 Daltons was prepared in a lab setting by a method as disclosed in copending applications US 20110178226 A1 and US

20110130520. Styrene monomer was fed at a rate of 2.98 g/min over a time of about 140 minutes into a reactor containing a mixture containing 185 grams of toluene, 1.72 grams of butyl lithium catalyst and 7.54 grams of TMEDA (tetra methyldiethylamine) catalyst. The reaction mass was kept near 0C for the duration of the reaction. The toluene was extracted by a wiped film evaporator and the polystyrene substrate was isolated and collected.

[0042] The substrate was then brominated. Bromine and dissolved polystyrene substrate were co-fed into a reactor containing 1384 grams of bromochloromethane solvent and 2.0 grams of aluminum chloride catalyst. Bromine was co-fed at a rate of 3.56 grams per minute along with a solution of the polystyrene substrate dissolved in bromochloromethane (35 wt% substrate in bromochloromethane) which was fed at a rate of 1.84 grams per minute. The reactor was kept at 0 C and constantly stirred. The feed took 3 hours and constant flow rates were maintained throughout. The bromine to polystyrene ratio fed was approximately 5.5. The bromine to catalyst ratio was approximately 440 grams of bromine per gram of catalyst.

[0043] The substrate was brominated under the conditions found in a commercial plant, and thus no sieve exposure pretreatment was carried out. The volume ratio of organic to water was 4.5, the product concentration was about 30%, i.e., at the end of the reaction, the reaction mass was 30% product and 70% solvent, disregarding any impurities.

[0044] Upon quenching the bromination reaction mass, the organic phase was observed to have a high degree of emulsion formation which comprises a high amount of entrained water. The wash efficiency (i.e., the wt% HBr in the aqueous phase after quenching)/(the wt% HBr in the aqueous phase after washing)) measures the degree of HBr extraction into the aqueous layer introduced with the quench step. In essence, it measures the amount of water entrained in the emulsified organic phase relative to the amount of water introduced in the quench step. Water which is not entrained is removed with the wash. The wash efficiency was 11.72. Thus, (1/11.72) or 8.5% of the water, and thus 8.5 % of the HBr, was entrained in the organic phase. This example is a laboratory demonstration of the emulsion formation observed on a commercial scale. **Fig. 1** is a photograph of the emulsion and aqueous phases observed. The reaction work-up includes an emulsified organic phase containing brominated polystyrene, bromochloromethane solvent, and an entrained aqueous phase which in itself contains hydrogen bromide, other ionics, and other impurities (milky lower layer). The funnel also contains a residual aqueous phase (upper layer) which contains the same components as the entrained aqueous phase.

Example 2

Observation of emulsion suppression in polystyrene polymers formed on a laboratory scale

[0045] In this example, emulsion formation is highly reduced, if not entirely eliminated, with molecular sieve particulate exposure according to the invention. Unbrominated polystyrene substrate from the same production batch as that used in Example 1 and brominated in the same conditions of Example 1 (organic to water ratio of 4.5, 30% product concentration, reagent ratios) was used in this example. However, the substrate solution in bromochloromethane (prior to bromination) was stirred after an addition of 5 wt% of 4A molecular sieves for about 12 hours. The sieves were then separated from the reaction mass via filtration through a medium porosity Buchner funnel and the polystyrene in BCM was then subjected to the bromination and quenching steps as in Example 1. After quenching, unlike the sample of Example 1, the organic layer was essentially clear (as can be seen in **Fig. 2**), and unlike example 1, no traces of emulsion were visibly detected. The wash efficiency for this Example was 56.96, which means that only 1.8 wt% of the available water was entrained in the organic phase, compared to 8.5 wt% in Example 1. The reduction in the relative partitioning with respect to water also holds with respect to the HBr in the sample.

[0046] The above two examples demonstrate that by including a molecular sieve treatment, less water, thus less water-soluble contamination, acid, and ultimately less ionics (H+, Br-, Na+ and OH-) are retained as part of an emulsion. This allows numerous process/procedural improvements, such as simplification of washing, leading to efficiencies such as lower cycle time and lower reagent use.

Example 3

Scale-up to pilot scale for the molecular sieve treatment

[0047] Polystyrene substrate that was produced using the same procedures as Examples 1 and 2 was used to test the molecular sieve treatment effectiveness at the pilot scale, a scale of approximately 100x in volume increase. Similar to Example 2, an amount of molecular sieves in excess of 2 wt % (relative to polystyrene) was used to treat the substrate material. However, one difference from Example 2 is that the agitation was done to replicate typical plant industrial agitation, and was performed by using a pump to pump the polystyrene substrate through a column of molecular sieves. Since the sieves were forced to remain in the column, no filtration through a Buchner funnel was necessary to isolate the polystyrene solution. The bromination proceeded with the same ratios and

methods described in Examples 1 and 2 except that it was being performed with industrial equipment, meaning the feed deliveries in this case were pressure transfer instead of being pumped, as well as the rest of the equipment being larger, impacting mixing dynamics.

[0048] After quenching the bromination reaction, the organic layer appeared very clear similar to Example 2. The wash efficiency was determined to be 58.06, or 1.7% of the available water was entrained in the organic phase. This example demonstrates the feasibility of scaling up the 4A mol sieve treatment to at least the pilot scale. Note that lab scale treatment and pilot scale treatment achieved nearly identical wash efficiencies (56.96 vs. 58.06).

Example 4

Optimization of molecular sieve loading for effective substrate treatment

[0049] The experiments of this example were conducted at both the lab scale and the pilot scale. The purpose of the experiments was to determine the optimal loading (i.e., the relative weight ratio of molecular sieves to polystyrene substrate) for molecular sieve treatment of the polystyrene solutions available. For the lab scale, the polystyrene substrate was prepared in the same manner as the substrate in Examples 1 and 2. For the pilot scale the polystyrene substrate was prepared in the same manner the substrate in Example 3. The brominations were also carried out in the same manner as Examples 1, 2 and 3. However, in this example, the molecular sieve loading used in the treatment step of the polystyrene substrate was different than that of Examples 2 and 3. Examples 2 and 3 were conducted with an amount of molecular sieves in excess of >2 wt %. The molecular sieve treatment of the present example was performed with a loading of 1 wt% relative to the polystyrene. The resulting wash efficiency was 50.91, or 2.0% of the available water was entrained in the organic phase, which is comparable to Examples 2 and 3 (56.96/1.8% and 58.06/1.7% respectively), demonstrating that 1% loading is an effective molecular sieve treatment for this system.

[0050] Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, a solvent, or *etc.*). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for

pursuant to this disclosure. Thus the components are identified as ingredients to be brought together in connection with performing a desired operation or in forming a desired composition. Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", *etc.*), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if conducted in accordance with this disclosure and with ordinary skill of a chemist, is thus of no practical concern.

[0051] Except where otherwise explicitly stated in this document, the invention may comprise, consist, or consist essentially of the materials and/or procedures recited herein.

[0052] As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods; and the like. The term about also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

[0053] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description or a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0054] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove.

CLAIMS:

1. A method for preventing the formation of a polystyrene emulsion, said method comprising the following steps:

1) providing a solution comprising polystyrene substrate which is dissolved in a halogenated alkane solvent or dissolving a polystyrene substrate in halogenated alkane solvent to form a dissolved polystyrene substrate solution;

2) contacting the dissolved polystyrene substrate solution of 1) with one or more molecular sieves;

3) separating the one or more molecular sieves from the dissolved polystyrene substrate solution such that the dissolved polystyrene substrate remains dissolved in the halogenated alkane solvent;

4) following the separation of step 3), contacting the dissolved polystyrene substrate solution with a bromination agent; wherein the contacting optionally occurs in the presence of a catalyst, such that the dissolved polystyrene substrate is brominated through a bromination reaction; and

5) contacting the brominated polystyrene substrate solution with an aqueous quenching reagent, thereby quenching the bromination reaction.

2. A method as in claim 1 wherein said sieves have an average pore size in the range of from about 2 to about 12 Angstroms; and wherein said contacting occurs for a time in the range of about 1 to about 12 hours, and at a loading in the range of about 0.5 to about 5.0 wt% mol sieves relative to polystyrene.

3. A method as in claim 1 wherein the molecular sieves comprise 4A molecular sieves.

4. A method as in claim 3 wherein the sieves are 4A sieves and the loading is in the range of about 0.7 to about 1.5 wt%.

5. A method as in claim 1 wherein no visible polystyrene emulsion is present.

6. A method as in claim 1 wherein the WE is in the range of about 20 to about 100.

7. A method as in claim 1 wherein the Mw of the polystyrene substrate is above about 650 Daltons.

8. A method as in claim 1 wherein the Mn of the polystyrene substrate is above about 500 Daltons.

9. A method as in claim 1 wherein the M_w and M_n of the polystyrene substrate is in the range of about 650 to about 750 and about 500 to about 600, respectively.

10. A method as in claim 1 wherein the alkane solvent is selected from the group consisting of chloromethane, bromomethane, bromochloromethane, dibromomethane and dichloromethane.

11. A method as in claim 1 wherein the alkane solvent comprises bromochloromethane.

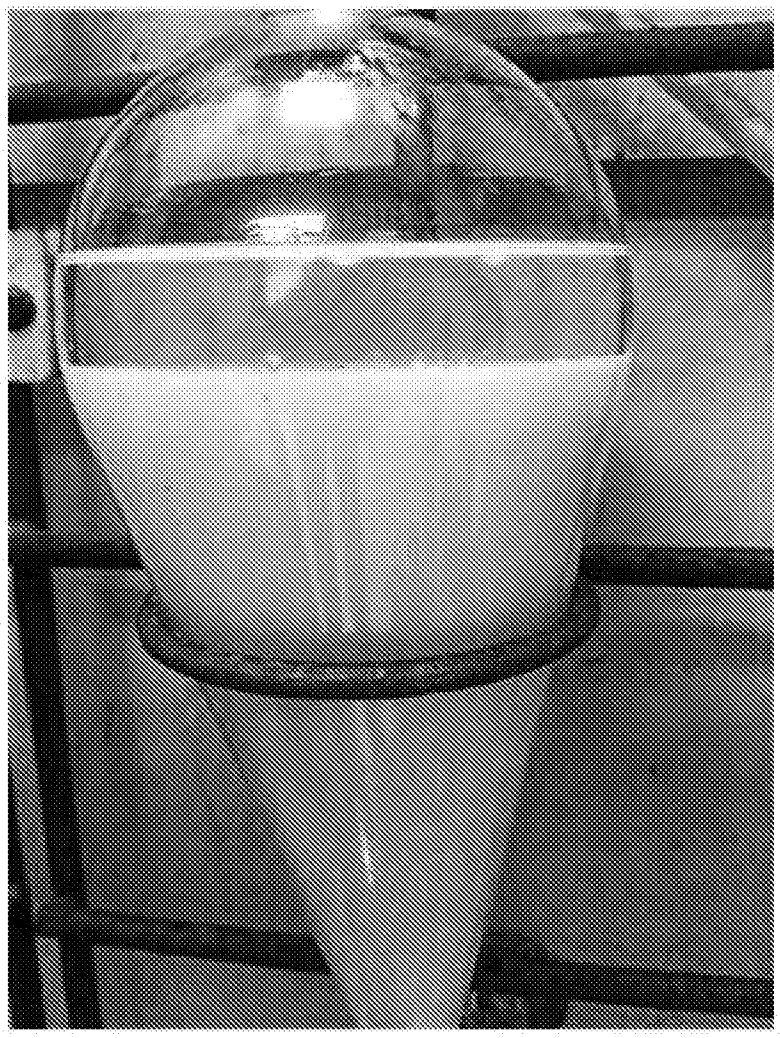

FIG. 1

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/076335

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F8/20 C08F6/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/061983 A1 (KOLICH CHARLES H [US] ET AL) 23 May 2002 (2002-05-23) paragraph [0118]	1-11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 March 2014	19/03/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Friebe, Lars

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/076335

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002061983 A1	23-05-2002	CA 2443288 A1	19-09-2002
		DE 60220386 T2	24-01-2008
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