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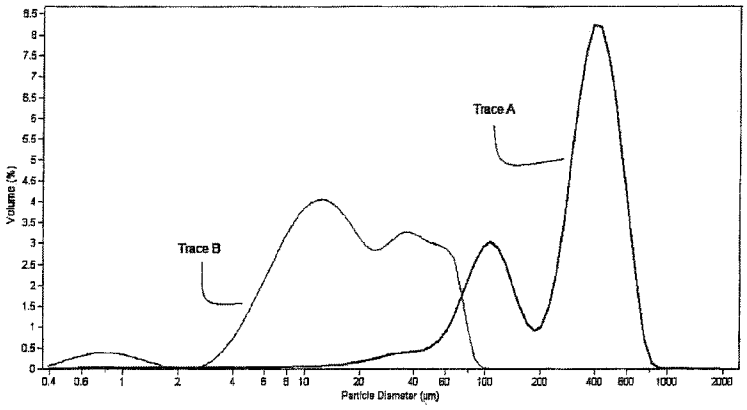

Fig. 1

(57) Abstract: Essentially dust-free particulate octylated phenyl-alpha-naphthylamine antioxidant and particle size enhancement methods for its formation are described. Such products avoid potential adverse health concerns and explosive hazards during handling and usage of the product. Also, methods for recovering high yields of particulate octylated phenyl-alpha- naphthylamine from crude octylated phenyl-alpha-naphthylamine product mixtures formed by catalytic alkylation of phenyl-alpha-naphthylamine with diisobutylene are described.

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LOW-DUST OCTYLATED PHENYL-ALPHA-NAPHTHYLAMINES AND FORMATION THEREOF

BACKGROUND

[0001] Octylated phenyl-alpha-naphthylamine is available as an article of commerce. It is an effective antioxidant for use in various substrates normally susceptible to oxidative degradation. including gas turbine fuels, oils and lubricants. The commercial product is available in the form of a light tan powder. As produced and when in dry form, octylated phenyl-naphthylamine is capable of producing finely-divided dusts during handling and usage.

[0002] The preparation of octylated phenyl-alpha-naphthylamine by catalytic alkylation of phenyl-alpha-naphthylamine with diisobutylene is described in U.S. Pat. No. 3,414,618. The patent reports a yield of 62% of theoretical.

[0003] A web page article on health effect of particles (Genano Ltd.; http://www.genano.fi/default.asp?id=2644) in part states as follows:

> "When considering the health effects of particles, particle size is the key factor. Particles more than 10µm in diameter do not get as far as the lungs, as they are normally caught in the nasal cavity and the pharynx. Particles smaller than 10µm may enter the upper respiratory tract just under the pharynx, where some of them are caught and removed (by coughing, spitting or swallowing). Particles smaller than 5µm may enter the bronchi in the upper lungs, while particles smaller than 2.5µm may get deep into the pulmonary alveoli where carbon dioxide in the blood is exchanged for oxygen. These particles are extremely hazardous, because the human lung has no efficient method of removing them."

This article further indicates that if these particles are smaller than 2.5µm and are water-soluble, they may enter the blood circulation in a matter of minutes, and if they do not dissolve in water, they may accumulate deep inside the lungs.

[0004] Organic particles of less than about 10 microns in size can remain suspended in the atmosphere for various periods of time, and thus pose a potential explosion hazard. As a general rule, the smaller the particles, the greater the explosion hazard.

[0005] It would be desirable to find a way of providing a low-dust octylated phenyl-alpha-naphthylamine product composition characterized by having low levels of "fines" – *i.e.*, particles having diameters of less than 10 microns, without recourse to screening or other similar procedures which in themselves tend to produce dusts. It would also be desirable to find a way of recovering particulate octylated phenyl-alpha-naphthylamine in

high yields (e.g., yields in the range of 80-95%) from a crude catalytically-octylated phenyl-alpha-naphthylamine product mixture having a content of octylated phenyl-alpha-naphthylamine in the range of about 80 to 98 GC area %. Such crude octylated phenyl-alpha-naphthylamine product mixtures formed by catalytic alkylation of phenyl-alpha-naphthylamine with diisobutylene are typically in the form of thick, viscous oily liquids, or in the form of solid chunks, flakes, or other solid aggregates. It would be especially desirable if the high yield recovery of octylated phenyl-alpha-naphthylamine from such crude product mixtures could also result is formation of a low-dust particulate octylated phenyl-alpha-naphthylamine product characterized by having low levels of "fines" sized in the range of 10 microns or less.

[0006] This invention is deemed capable of achieving these desirable objectives in an economical, industrially-feasible manner.

BRIEF NON-LIMITING SUMMARY OF THE INVENTION

[0007] This invention is deemed to reduce considerably, if not virtually eliminate, the foregoing concerns as regards potential inhalation effects and potential explosion hazards with respect to octylated phenyl-alpha-naphthylamine. This is accomplished by providing low-dust octylated phenyl-alpha-naphthylamines and methods for forming them. This invention also enables recovery of particulate octylated phenyl-alpha-naphthylamine in high yields from a crude octylated phenyl-alpha-naphthylamine product mixture formed by catalytic alkylation of phenyl alpha-naphthylamine with diisobutylene. Such crude octylated phenyl-alpha-naphthylamine product mixtures formed by catalytic alkylation of phenyl-alpha-naphthylamine with diisobutylene are typically in the form of thick, viscous oily liquids, or in the form of solid chunks, flakes, or other solid aggregates.

[0008] Octylated phenyl-alpha-naphthylamine may also be referred to by the following alternative names:

N-[4-(1,1,3,3-tetramethylbutyl)phenyl]-1-naphthalenamine;

N-[(1,1,3,3-tetramethylbutyl)phenyl]-1-naphthalenamine;

1-phenyl-*ar*-(1,1,3,3-tetramethylbutyl)-naphthalenamine;

N-(4-tert-octylphenyl)-1-naphthylamine.

[0009] Other features and aspects of this invention will be apparent from the ensuing description, accompanying drawing, and appended claims.

BRIEF DESCRIPTION OF THE DRAWING

[0010] Fig. 1 is a comparative graphical presentation of particle size distributions of a sample of octylated phenyl-alpha-naphthylamine product of this invention and of a sample of a commercially-available octylated phenyl-alpha-naphthylamine which is in the form of a powder.

[0011] Fig. 2 is a comparative graphical presentation of particle size distributions of a sample of another octylated phenyl-alpha-naphthylamine product of this invention and of a sample of a commercially-available octylated phenyl-alpha-naphthylamine which is in the form of a powder.

[0012] Figs. 3-11 are graphical presentations of results of particle size distribution of other samples of octylated phenyl-alpha-naphthylamines of, and formed by the particle size enhancement methods of, this invention.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

[0013] This invention provides, among other things, a particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than about 20% by volume of the particles have a diameter of less than 10 microns. In a preferred embodiment, the foregoing particulate antioxidant is additionally characterized in that less than 5% by volume of the particles have a diameter of less than 5 microns. In a still further preferred embodiment, the foregoing particulate antioxidant is still further characterized in that less than 3% by volume of the particles have a diameter of less than 2.5 microns.

[0014] A further embodiment of this invention is a particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than 5% by volume of the particles have a diameter of less than 5 microns. Preferably, this antioxidant is also characterized in that less than 3% by volume of the particles have a diameter of less than 2.5 microns.

[0015] A still further preferred embodiment of this invention is a particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than 3% by volume of the particles have a diameter of less than 2.5 microns.

[0016] It is to be noted that use of the term "diameter" in connection with particle size measurements does not denote that the particle must be in spherical shape. The word "diameter" is simply used to denote the largest cross-sectional size of the particles. The word "size" applies equally well since reference is being made to the maximum dimension of the

particle. A procedure for carrying out a determination of such particle size distributions and histograms and plots of such distributions is presented hereinafter.

[0017] Also provided by this invention, *inter alia*, are methods of recovering particulate octylated phenyl-alpha-naphthylamine antioxidant in high yields (*e.g.*, yields in the range of 80-98%) from a crude octylated phenyl-alpha-naphthylamine product mixture formed by catalytic alkylation of phenyl-alpha-naphthylamine with diisobutylene. Such a method comprises:

- crystallizing said crude octylated phenyl-alpha-naphthylamine product mixture in a crystallization medium composed of liquid alkanol or a single phase liquid mixture of alkanol and water;
- recovering crystallized octylated phenyl-alpha-naphthylamine from the crystallization medium;
- optionally recrystallizing such recovered crystallized octylated phenyl-alpha-naphthylamine in a crystallization medium composed of liquid alkanol or a single phase liquid mixture of alkanol and water, and recovering recrystallized octylated phenyl-alpha-naphthylamine from the crystallization medium; and
- drying recovered crystallized octylated phenyl-alpha-naphthylamine product.

As noted above, such crude product mixtures subjected to the foregoing recovery process are typically in the form of either thick, viscous oily liquids, or in the form of solid chunks, flakes, or other solid aggregates. In conducting this method, any liquid primary, secondary and/or tertiary alkanol, or any single phase liquid mixture of primary, secondary, and/or tertiary alkanol and water, can be used as the crystallization medium. Preferably, a liquid secondary alkanol or a single phase liquid mixture of a secondary alkanol and water is used as the crystallization medium. The secondary alcohols, isopropyl alcohol and secondary butyl alcohol, have been found to give excellent results in the practice of this method.

[0018] In preferred forms, the foregoing recovery methods form and recover products such as the following:

a) a particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than about 20% by volume of the particles have a diameter of less than 10 microns;

b) a particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than 5% by volume of the particles have a diameter less

than 5 microns; and/or

c) a particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than 3% by volume of the particles have a diameter of less than 2.5 microns.

[0019] For particle size determinations, the particles should be dry. As used herein, the term "dry" denotes that the product has a water content of no more than 0.1 wt% by the Karl Fischer or equivalent test method, and is otherwise not wetted by any other solvent or diluent.

Synthesis of Octylated Phenyl-Alpha-Naphthylamine

[0020] An important feature of this invention is the crude octylated phenyl-alpha-naphthylamine which is treated pursuant to this invention can be formed by any known method for catalytically alkylating phenyl-alpha-naphthylamine with diisobutylene. In other words, it matters not what kind of suitable catalyst is used in the alkylation reaction producing the octylated product. Such catalysts are typically a Lewis acid catalyst such as aluminum chloride, diethylaluminum chloride, ethylaluminum sesquihalide, ethylaluminumdichloride, ethylaluminumdichloride/HCl, triethylaluminum/3HCl, diethylaluminumchloride/2HCl, and the like. Acidic clays are still additional known catalysts for carrying out such alkylations. The alkylation reactions are typically conducted at temperatures at about 70 to about 110°C. The crude octylated phenyl-alpha-naphthylamine product mixtures formed by catalytic alkylation of phenyl-alpha-naphthylamine with diisobutylene typically comprises at least octylated phenyl-alpha-naphthylamine and phenyl-alpha-naphthylamine, and additionally often comprises some butylated phenyl-alpha-naphthylamine and/or some dioctylated phenyl-alpha-naphthylamine and/or some diisobutylene dimer.

[0021] Pursuant to the particle size enhancement aspects of this invention and the preferred embodiments of the high yield recovery aspects of this invention, the crude octylated phenyl-alpha-naphthylamine is subjected to processing which provides a particle distribution in which dust-forming particles are essentially eliminated from the crude product. The processing used involves crystallization from an aqueous or essentially anhydrous liquid alkanol, especially aqueous or essentially anhydrous secondary alkanol such as sec-butyl alcohol, and more preferably aqueous or essentially anhydrous isopropyl alcohol, since the final product can be obtained therefrom in a form which has particle size distributions as

described above. For example, as will be seen from experimental results conducted on a laboratory scale, particulate antioxidants of this invention in which less than 0.75% by volume of the particles have a diameter of less than 5 microns, and particulate antioxidants of this invention in which less than 0.75% by volume of the particles have a diameter of less than 2.5 microns were produced by use of a particle size enhancement method of this invention. Indeed, and as also shown by experimental results presented hereinafter, when conducting particle size enhancement methods of this invention, it was possible to form octylated phenyl-alpha-naphthylamine products of this invention having less than 0.5 % by volume of particles of less than 5 microns in size and less than 0.25 % by volume of particles of less than 2.5 microns in size. It is therefore not inconceivable that products may be formed using particle size enhancement methods of this invention with repeated crystallizations in which there is essentially no detectable amount of particles of less than 5 microns in size.

[0022] The crystallization step or steps can be conducted at any suitable temperatures at which the desired product crystallizes from the liquid crystallization medium. In general, such temperature or temperatures may be any suitable temperature in the range of (i) a temperature somewhat below the melting temperature of the particular octylated phenyl-alpha-naphthylamine product being crystallized and (ii) a temperature somewhat above the freezing temperature of the liquid crystallization medium being employed. Ordinarily, the crystallization(s) will be carried out at temperatures below the atmospheric boiling temperature of the liquid crystallization medium being employed, although the crystallization medium can be carried under elevated pressure to prevent boiling, if desired. For convenience, crystallization is usually conducted at one or more temperatures in the range of about 0 to about 70°C and preferably in the range of about 30 to about 65°C.

[0023] The volume ratio of alkanol to water used in the crystallization step may range from about 60:40 to 100:0. It is preferred to use ratios within the foregoing range that have a relatively high ratio of water to alkanol as this generally produces high recovered yields of purified octylated phenyl-alpha-naphthylamine. However, amount of water yielding ratios in which the water proportion is greater than 40 results in high levels of impurities in the purified octylated phenyl-alpha-naphthylamine and will also result in the formation of fine particles. Such levels of water in a proportion of greater than 40 may also cause the octylated phenyl-alpha-naphthylamine to "oil out" and thus completely prevent the formation of a crystalline product. Most preferred is an alkanol:water ratio of 80:20 to 65:35. As can be

seen from the accompanying drawings, it is possible, depending upon the proportions of the components used in the crystallization step, to form either bimodal or monomodal product distributions. The temperatures at which the crystallization is conducted depends somewhat upon the composition (*e.g.*, nature and content of impurities) of the specific octylated phenyl-alpha-naphthylamine being treated. Generally speaking, one or a range of temperatures up to the melting point of the particular octylated phenyl-alpha-naphthylamine can be used, provided the crystallization medium remains as a single phase liquid medium. Ideally the starting temperature of the crystallization should be high enough so that all of the octylated phenyl-alpha-naphthylamine component(s) dissolve in the crystallization medium. Once the product has been crystallized, it is recovered from the crystallization medium, *e.g.*, by filtration, centrifugation, decantation, or other suitable liquids-solids separation procedure, optionally is washed, and then is dried to afford the final crystallized octylated phenyl-alpha-naphthylamine product of this invention. At least when isopropyl alcohol is the alkanol used alone or with water in a particle size enhancement method of this invention, air drying can be used, *e.g.*, by exposing the product at ambient temperature to a flow of air or inert gas such as nitrogen, but preferably the recovered product is dried at a suitable relatively mild elevated temperature, such as up to about 50-60°C. Somewhat higher temperatures may be used if desired, provided that such higher temperatures do not result in melting of the product, which has a melting point of about 77°C, or in prolonged exposure to the product to air at such higher temperatures. To control cost and reduce undesirable waste, it is preferred to carry out only one crystallization of crude octylated phenyl-alpha-naphthylamine, provided that one crystallization results in a particle size enhancement giving a product distribution with low amounts of fines pursuant to this invention. In some cases a single crystallization may not achieve the desired particle size distribution, presumably because the composition and impurity content of the initial octylated phenyl-alpha-naphthylamine being processed. Thus, if necessary to achieve the desired particle size distribution and elimination of "fines" from the product, a second crystallization, pursuant to this invention, may be used. Typically, no further crystallizations will be required but may be utilized should this prove necessary.

[0024] Although variations may prove feasible, the rate of crystallization of the crude octylated phenyl-alpha-naphthylamine product mixture is typically about 1°C or less per minute.

[0025] The methods of this invention for producing octylated phenyl-alpha-naphthylamine

products having desirable product distributions of this invention can be applied to octylated phenyl-alpha-naphthylamine reaction product as recovered as crude product from the alkylation reaction in which such product was formed. Alternatively, such methods can be applied to octylated phenyl-alpha-naphthylamine which has already been purified by other methods but which, because of its content of "fines", is capable of producing undesirable amounts of dusts and thus does not have a desirable particle size distribution characterizing a product of this invention. To control cost and reduce undesirable waste it is preferred to carry out only one crystallization of crude octylated phenyl-alpha-naphthylamine, provided that one crystallization results in a high product yield of this invention and/or a particle size enhancement giving a product distribution with low amounts of fines pursuant to this invention.

Determination of Particle Size Distribution

[0026] To assay the particle size distribution of octylated phenyl-alpha-naphthylamine samples, the particle size distributions are measured as liquid suspensions using a Coulter LS230 Particle Size Analyzer or equivalent. The procedure used is as follows:

[0027] Sample preparation involves placing 200 mg of the sample in a 20 mL vial. To the sample is added 3 mL of 1 wt % Triton-X 100™ surfactant in water, and the mixture is shaken. An ultrasonic probe is then placed in the suspension and energized for 5 seconds. This produces a stable, well dispersed suspension that is ready for measurement of the particle size distribution (PSD). A recirculation cell of approximately 150 mL volume is filled with 1 wt % Tween 80 surfactant solution in water. The LS230 background data is obtained while this solution is circulated through the cell. The sample suspension is then slowly added while monitoring the detector array reading until the proper level of light scattering is obtained. The resulting sample suspension is then circulated through the cell for 60 seconds while the outputs of the angular diffraction (for larger particles) and polarized scattering (for smaller particles) detectors are recorded and stored to a raw data file. After the measurement is complete, the LS230 instrument analyzes the diffraction and scattering data and computes a distribution of particle sizes. The PSD plots reported for this measurement have this particle size in microns as the X-axis and volume % as the Y-axis. The volume % is the directly measured intensity variable in the PSD because the scattering particle will be rotating about all three spatial coordinate axes while the particle is being measured. Hence the volume in space that it sweeps out is the parameter that correlates with

the intensity measurements. If the particle density is independent of size (the usual assumption) then the volume % is equal to the weight %.

[0028] The following Examples are presented for purposes of illustration. These Examples are not intended to constitute limits on the scope or practice of this invention.

[0029] Example 1 illustrates the high yield recovery aspects coupled with the particle size enhancement aspects of this invention.

EXAMPLE 1

[0030] Into a 5L jacketed round bottom flask equipped with nitrogen pad, overhead stirrer, and thermowell was charged 1272g of crude octylated-phenyl-alpha-naphthylamine produced by alkylation of phenyl-alpha-naphthylamine with diisobutylene using aluminum chloride as catalyst. To this crude product 2397g of a 85 wt.% solution of isopropyl alcohol in water was added and the mixture was heated to >65°C to dissolve all of the solids and to form a single liquid phase. Optionally, a small amount of sodium borohydride or similar reducing agent may be added at this point to improve coloration of the final product, should this be desired. Once at temperature, the mixture is slowly cooled until the pot temperature is <40°C. Seed crystals may be added during the cool down to induce nucleation. Once at <40°C, 435g of water was added over 30 minutes to bring the overall ratio of isopropyl alcohol to water to 72:28 w/w to improve the isolated yield of octylated phenyl-alpha-naphthylamine. The mixture was filtered, washed with 60:40 w/w isopropyl alcohol:water, and then vacuum dried at 50°C to afford 1101g crystallized octylated phenyl-alpha-naphthylamine (97.0 wt.% via internal standard, 97.9 wt.% upon normalization of sample; 90.8% molar yield from starting PANA after accounting for analytical samples removed during process). Coloration was off white to pinkish. Morphology = small spheroids.

[0031] A representative sample of this product from Example 1 was subjected to particle size distribution analysis using the Coulter LS230 procedure described above. For comparison, a sample of commercially-available octylated phenyl-naphthylamine powder was also subjected to such particle size distribution analysis. Results of these comparative particle size determinations are depicted in Fig. 1. It is of interest that the commercially-available powdery product contained about 31.7 volume % of particles of less than 10 microns in size, about 10.1 volume percent of particles of less than 5 microns in size and about 4.2 volume percent of particles of less than 2.5 microns in size, whereas the product of this invention from Example 1 contained about 0.83 volume percent of particles of less than

10 microns in size, about 0.52 volume percent of particles of less than 5 microns in size and about 0.34 volume percent of particles of less than 2.5 microns in size.

[0032] Examples 2 and 3 illustrate particle size enhancement methods of this invention wherein different ratios and amounts of crude octylated phenyl-naphthylamine and crystallization media were used.

EXAMPLE 2

[0033] Four crude samples of octylated phenyl-alpha-naphthylamine of a purity of ~85.0 wt% were treated pursuant to the particle size enhancement aspects of this invention by crystallization in different mixtures of isopropyl alcohol (IPA) and water. The operations were carried out by heating individual 40 gram samples of such crude octylated phenyl-alpha-naphthylamine in each individual selected isopropyl alcohol/water crystallization medium to a temperature at which complete solution was effected. The samples were then allowed to cool and the resulting crystallized solids were filtered, air-dried, and then analyzed by GC for purity, melting point, and particle size. The results of these operations are summarized in Table 1 in which OPANA denotes octylated phenyl-alpha-naphthylamine and PANA denotes phenyl-alpha-naphthylamine. Particle size distributions were measured for these samples by use of the Coulter LS230 Particle Size Analyzer in accordance with the procedure described above. Amounts of components used in the crystallizations and results of particle size distribution determinations are summarized in Table 1.

TABLE 1

Product Sample	A	B	C	D
Crystallization Medium	95 wt% IPA & 5 wt% water	95 wt% IPA & 5 wt% water	90 wt% IPA & 10 wt% water	75 wt% IPA & 25 wt% water
Starting crude (g)	40	40	40	40
Amt. of medium (g)	100	50	100	100
Isolated Product (g)	26.9	31.3	31.7	33.0
DSC mp (°C)	76.2	76.4	77.8	76.0
Wt% Recovery	67.3	78.2	79.3	82.5
Wt% pure OPANA	93.0	95.0	96.0	95.2
Wt% PANA	1.4	1.5	1.3	1.4
Particle Size Determinations				
Avg. size (microns)	304	245	736	195
Vol.% of <10 microns	1.01	2.57	0.27	0.54
Vol.% of <5 microns	0.56	0.91	0.17	0.20
Vol.% of <2.5 microns	0.31	0.55	0.09	0.03

EXAMPLE 3

[0034] Five crude samples of octylated phenyl-alpha-naphthylamine of a purity of ~84 wt% were treated pursuant to the particle size enhancement aspects of this invention by crystallization in different crystallization media used pursuant to this invention. The operations were carried out by heating individual 40 gram samples of such crude octylated phenyl-alpha-naphthylamine in each individual selected crystallization medium (either isopropyl alcohol or sec-butyl alcohol) to a temperature at which complete solution was effected. The samples were then allowed to cool and the resulting crystallized solids were filtered and air-dried overnight. GC area % analysis was utilized to determine the purity of the isolated product. Average particle size was also determined by use of the Coulter LS230 procedure described above. Results of these operations are summarized in Table 2 in which s-BuOH denotes sec-butyl alcohol and IPA denotes isopropyl alcohol. The designations OPANA and PANA are as in Example 2, and "RT" denotes room temperature.

TABLE 2

Product Sample	E	F	G	H	I
Crystallization Medium	s-BuOH	s-BuOH	IPA	IPA	IPA
Amt. of Medium (g)	50	100	50	100	100
Amt. of Crude OPANA (g)	40	40	40	40	40
Temperature Condition	RT	RT	RT	RT	Ice bath
Isolated crystallized product (g)	26.9	21.8	29.7	26.5	30.0
Recovery % based on crude	67.3	54.5	74.3	66.2	75.0
Wt.% OPANA in Product	96.7	98.1	95.8	97.2	93.3
Wt.% PANA in Product	1.6	1.1	1.6	1.7	3.3
Particle Size Determinations					
Avg. Particle Size (microns)	132	321	117	314	167
Vol.% of <10 micron particles	1.12	0.57	0.71	0.45	2.69
Vol.% of <5 micron particles	0.71	0.32	0.42	0.15	1.4
Vol.% of <2.5 micron particles	0.47	0.16	0.24	0.03	0.80

[0035] Example 4 provides another illustration of a high yield recovery aspect of this invention coupled with a particle size enhancement aspect of this invention. Thus, the method used not only crystallizes the product but eliminates undesirable quantities of "fines" therefrom.

EXAMPLE 4

[0036] A thick oily crude concentrated reaction mass (562 g) formed by catalytic alkylation of phenyl-alpha-naphthylamine with diisobutylene was dissolved in 800 g of 10% aqueous

isopropyl alcohol and then allowed to stand overnight to crystallize at room temperature. The resulting crystalline solid was filtered and rinsed with 300 g of 10% aqueous isopropyl alcohol. The resultant off white crystalline product was allowed to air dry over the weekend to obtain 455.2 g of crystallized octylated phenyl-alpha-naphthylamine product. Results of GC analyses of the crude product before crystallization and of the crystallized product are summarized in Table 3, and a summary of particle size distribution data as determined by use of the Coulter LS230 procedure is presented in Table 4. In Table 3, OPANA and PANA have the same meanings as in Example 3. The numerical values in Table 3 are GC area percentages.

TABLE 3

Wt.% of Components	Crude before Crystallization	Crystallized Product
PANA	5.2	0.38
OPANA	89.0	98.73

TABLE 4

Components	Result
90%	944.1 microns
75%	687.3 microns
50%	424.7 microns
25%	252.7 microns
10%	137.8 microns
Particle Size Range	0.721-1255 microns
Vol. % of Particles of <10 microns in size	0.47
Vol. % of Particles of <5 microns in size	0.30
Vol. % of Particles of <2.5 microns in size	0.18

[0037] Referring now to the drawings, Fig. 1 is a graphical presentation of the particle size distribution of a sample of octylated phenyl-alpha-naphthylamine product of this invention formed in Example 2 and for comparative purposes, a graphical presentation of the particle size distribution of a sample of a commercially-available octylated phenyl-alpha-naphthylamine which is in the form of a powder. Fig. 2 is another comparative graphical presentation of particle size distributions in which a sample of octylated phenyl-alpha-naphthylamine product of this invention formed in Example 4 is compared to the same sample of the commercially-available octylated phenyl-alpha-naphthylamine. Despite the reversals of the thicknesses of the trace lines as between Fig. 1 and Fig. 2, the curves marked "Trace A" are the particle size traces of the products of this invention whereas the curves

marked "Trace B" is the particle size trace of the commercially-available product.

[0038] Figs. 3-9 are graphical presentations of the particle size distribution of product samples of various other octylated naphthylamine products formed by the particle size enhancement methods of this invention and having particle sizes in accordance with this invention. These figures are depictions of histograms from a Coulter LS230 Particle Size Analyzer in which the curve made up of circles and dashes (◦–◦–◦–◦) depict the actual particle size measurements. The lighter curve composed of short dashed lines depicts the cumulative results of that particle size determination. Thus, Figs. 3-6 are depictions of histograms of product samples A-D, respectively, of Example 2, Table 1. Figs. 7-11 are depictions of histograms of product samples E-I, respectively, of Example 3, Table 2.

[0039] 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. 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.

[0040] The invention may comprise, consist or consist essentially of the materials and/or procedures recited herein.

[0041] 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 particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than about 20% by volume of the particles have a diameter of less than 10 microns.

2. An antioxidant as in Claim 1 in which said antioxidant is further characterized in that less than 5% by volume of the particles have a diameter of less than 5 microns.

3. An antioxidant as in Claim 1 in which said antioxidant is further characterized in that less than 3% by volume of the particles have a diameter of less than 2.5 microns.

4. An antioxidant as in Claim 1 in which said antioxidant is further characterized in that less than 5% by volume of the particles have a diameter of less than 5 microns and in which less than 3% by volume of the particles have a diameter of less than 2.5 microns.

5. A particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than about 5% by volume of the particles have a diameter of less than 5 microns.

6. A particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than about 3% by volume of the particles have a diameter of less than 2.5 microns.

7. A method of forming a particulate octylated phenyl-alpha-naphthylamine antioxidant having a particle size distribution in which less than about 20% by volume of the particles have a diameter of less than 10 microns which method comprises:

- crystallizing in a crystallization medium a crude octylated phenyl-alpha-naphthylamine product mixture formed by catalytic alkylation of phenyl-alpha-naphthylamine with diisobutylene, wherein said crystallization medium is composed of liquid alkanol or a single phase liquid mixture of alkanol and water;
- recovering crystallized octylated phenyl-alpha-naphthylamine from the crystallization medium;
- optionally recrystallizing such recovered crystallized octylated phenyl-alpha-naphthylamine in a crystallization medium composed of liquid alkanol or a single phase liquid mixture of alkanol and water, and recovering recrystallized octylated phenyl-alpha-naphthylamine from the crystallization medium; and
- drying recovered crystallized octylated phenyl-alpha-naphthylamine, said dried recovered crystallized phenyl alpha-naphthylamine having a particle size distribution in which less than about 20% by volume of the particles have a diameter of less than

10 microns.

8. A method as in Claim 7 further comprising washing crystallized octylated-phenyl-alpha-naphthylamine recovered from the crystallization medium with liquid alkanol or a single phase liquid mixture of alkanol and water prior to drying said recovered crystallized octylated-phenyl-alpha-naphthylamine.

9. A method as in any of Claims 7 or 8 wherein the product distribution of said dried recovered crystallized octylated phenyl-alpha-naphthylamine is further characterized in that less than 5% by volume of the particles have a diameter of less than 5 microns

10. A method as in Claim 9 wherein the product distribution of said dried recovered crystallized octylated phenyl-alpha-naphthylamine is further characterized in that less than 3% by volume of the particles have a diameter of less than 2.5 microns.

11. A method of recovering particulate octylated phenyl-alpha-naphthylamine antioxidant in high yields from a crude octylated phenyl-alpha-naphthylamine product mixture formed by catalytic alkylation of phenyl-alpha-naphthylamine with diisobutylene, which method comprises:

- crystallizing said crude octylated phenyl-alpha-naphthylamine product mixture in a crystallization medium composed of liquid alkanol or a single phase liquid mixture of alkanol and water;
- recovering crystallized octylated phenyl-alpha-naphthylamine from the crystallization medium;
- optionally recrystallizing such recovered crystallized octylated phenyl-alpha-naphthylamine in a crystallization medium composed of liquid alkanol or a single phase liquid mixture of alkanol and water, and recovering recrystallized octylated phenyl-alpha-naphthylamine from the crystallization medium; and
- drying recovered crystallized octylated phenyl-alpha-naphthylamine product.

12. A method as in Claim 11 further comprising washing crystallized octylated-phenyl-alpha-naphthylamine recovered from the crystallization medium with liquid alkanol or a single phase liquid mixture of alkanol and water prior to drying said recovered crystallized octylated-phenyl-alpha-naphthylamine.

13. A method as in any of Claims 7, 8, 11, or 12 wherein said crystallization medium is composed of a single phase liquid mixture of secondary alkanol and water in a secondary alkanol:water volume ratio in the range of about 60:40 to about 95:5.

14. A method as in Claim 13 wherein said secondary alkanol is isopropyl alcohol.

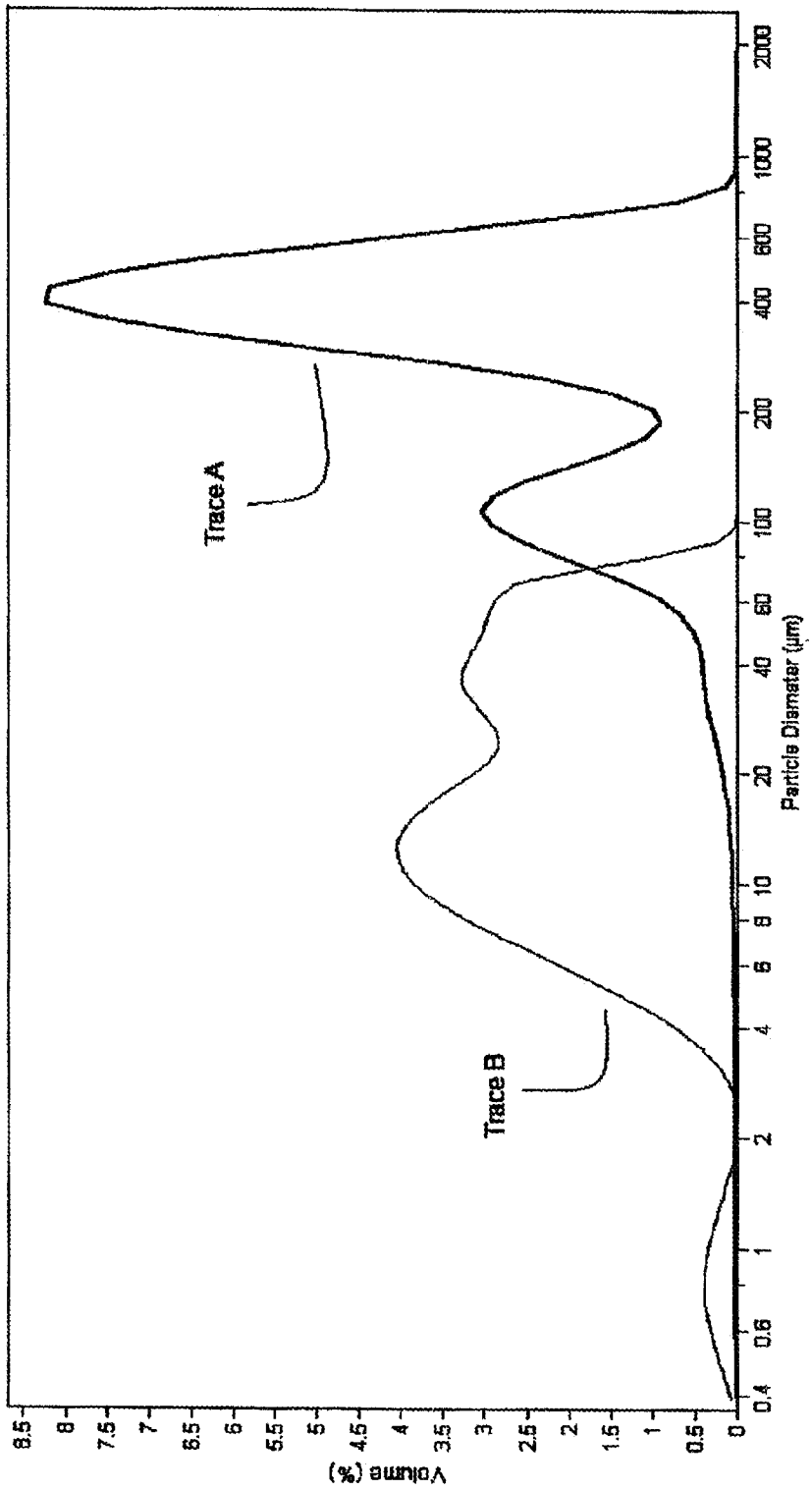
Trace A
Trace B
Volume (%)
Particle Diameter (µm)
0.4
0.6
1
2
4
6
8
10
20
40
60
100
200
400
600
1000
2000
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
8.5

Fig. 1

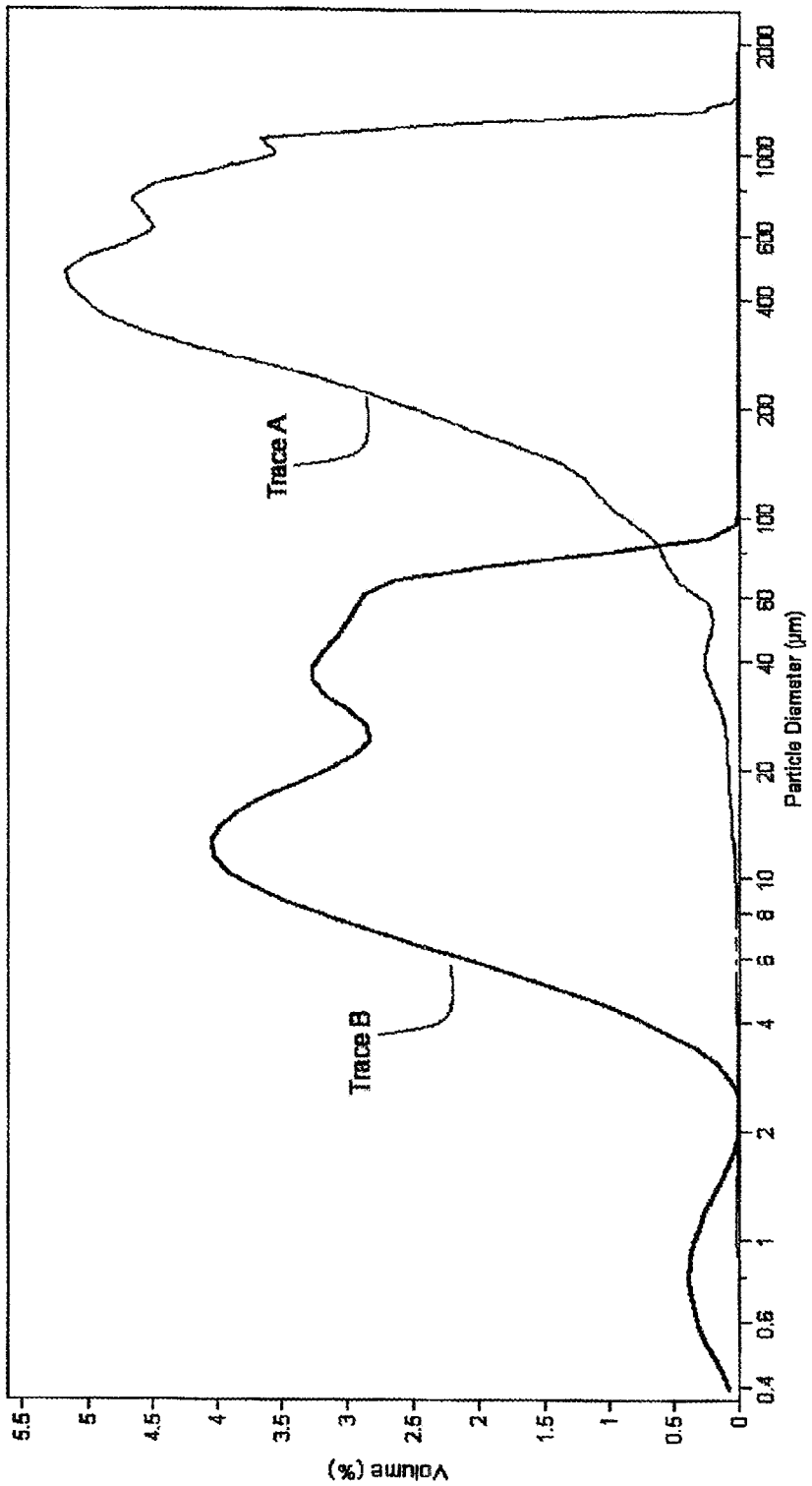
Volume (%)
Particle Diameter (µm)
Trace A
Trace B
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
0.4
0.6
1
2
4
6
8
10
20
40
80
100
200
400
600
1000
2000

Fig. 2

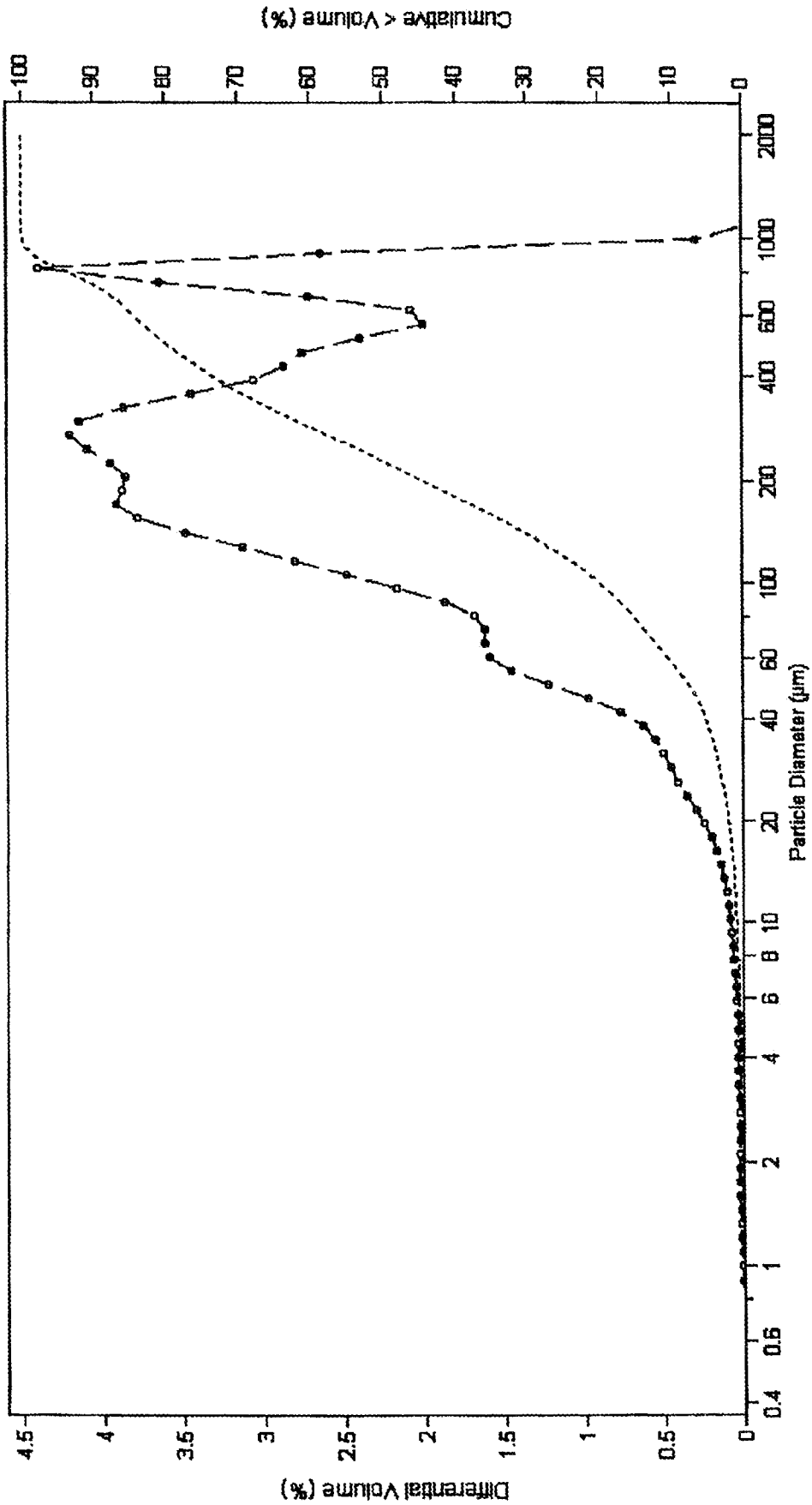
Cumulative < Volume (%)
100
90
80
70
60
50
40
30
20
10
0
Differential Volume (%)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0.4
0.6
1
2
4
6
8
10
20
40
60
100
200
400
600
1000
2000
Particle Diameter (µm)

Fig. 3

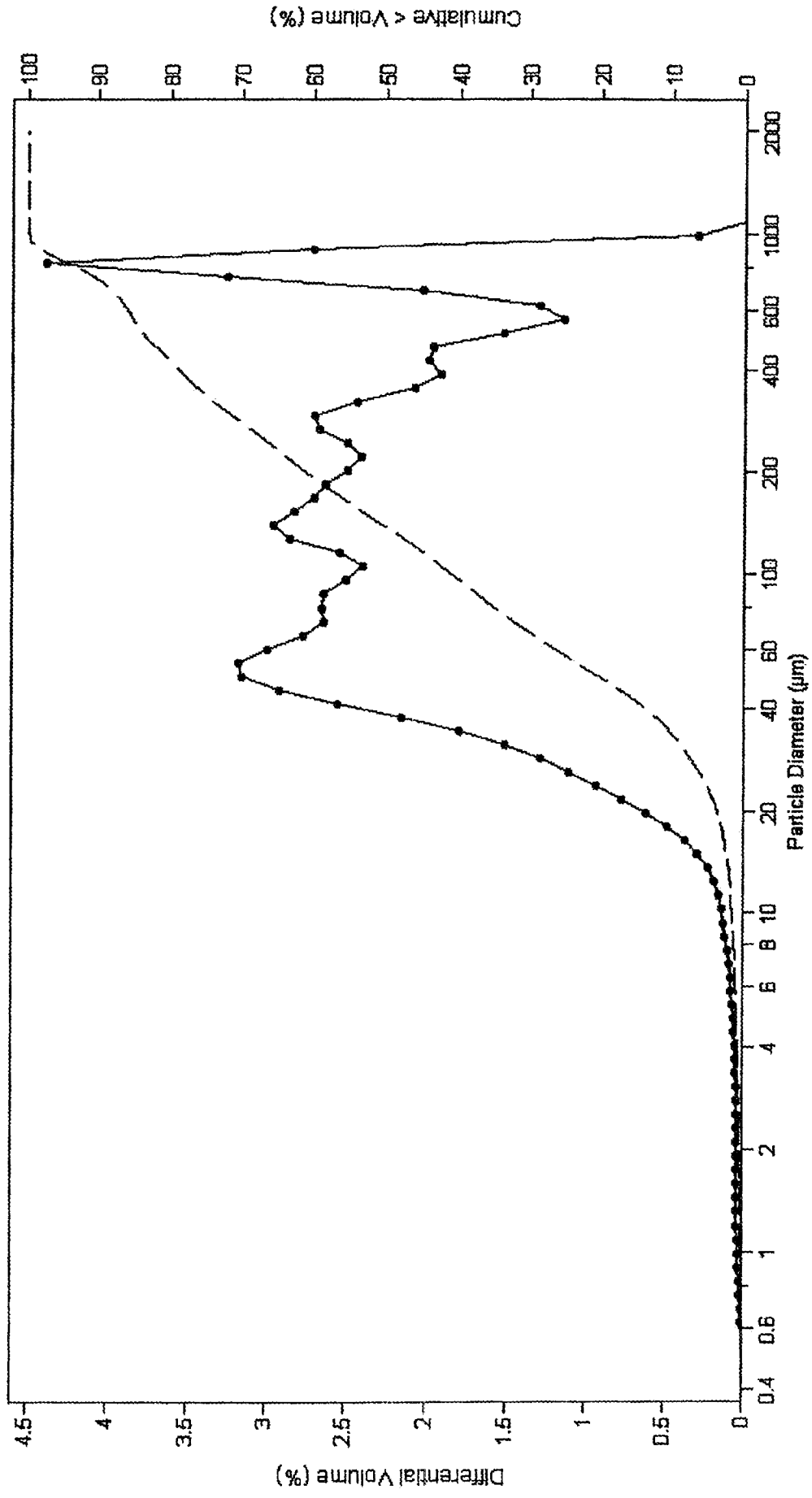
Differential Volume (%)
Cumulative < Volume (%)
Particle Diameter (µm)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
0
10
20
30
40
50
60
70
80
90
100
0.4
0.6
1
2
4
6
8
10
20
40
60
100
200
400
600
1000
2000

Fig. 4

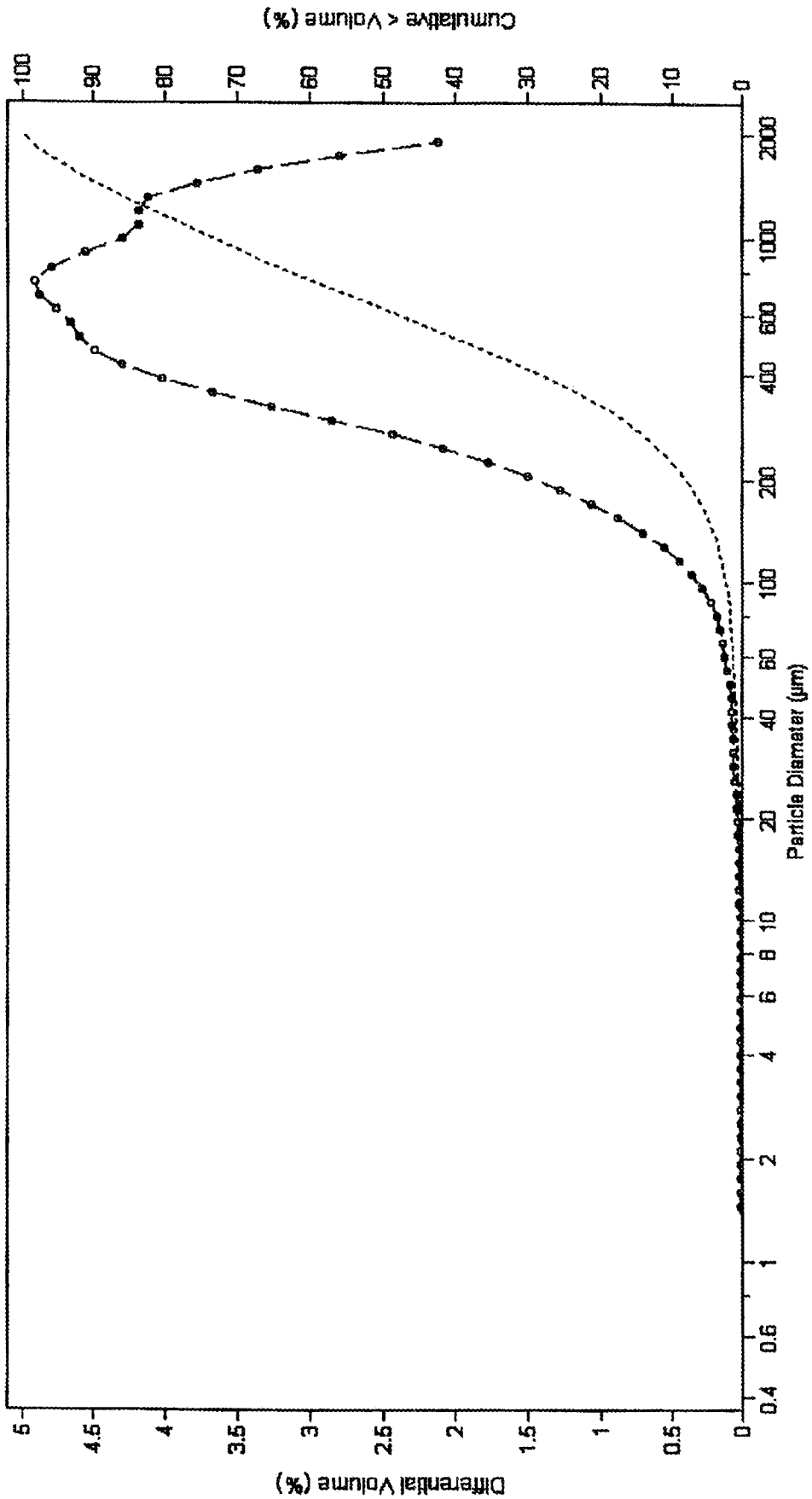
Cumulative < Volume (%)
100
90
80
70
60
50
40
30
20
10
0
2000
1000
600
400
200
100
80
60
40
20
10
8
6
4
2
1
0.6
0.4
Particle Diameter (µm)
Differential Volume (%)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0

Fig. 5

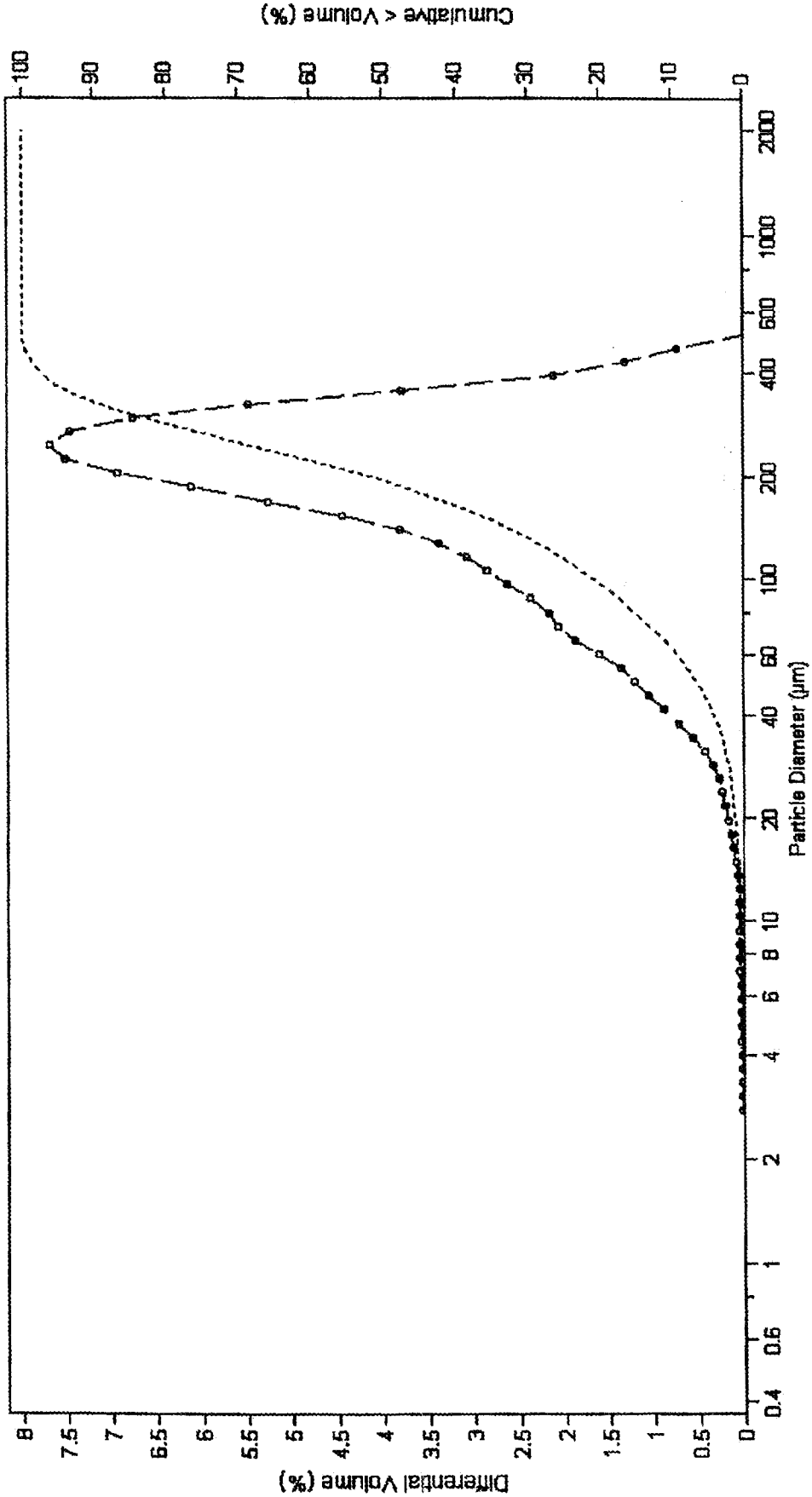
Cumulative < Volume (%)
Differential Volume (%)
Particle Diameter (µm)

Fig. 6

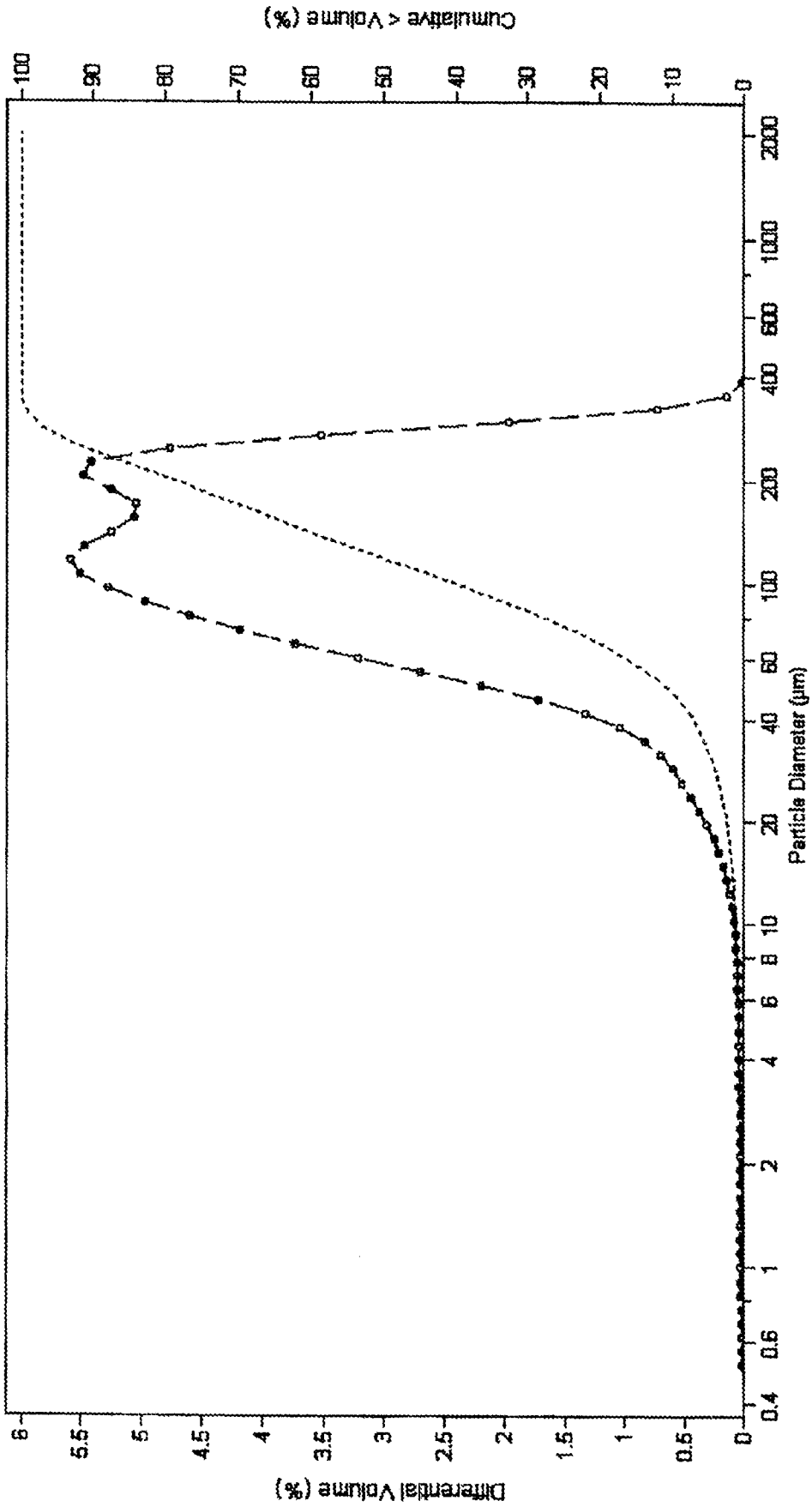
Cumulative < Volume (%)
100
90
80
70
60
50
40
30
20
10
0
Differential Volume (%)
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0.4
0.6
1
2
4
6
8
10
20
40
60
80
100
200
400
600
1000
2000
Particle Diameter (µm)

Fig. 7

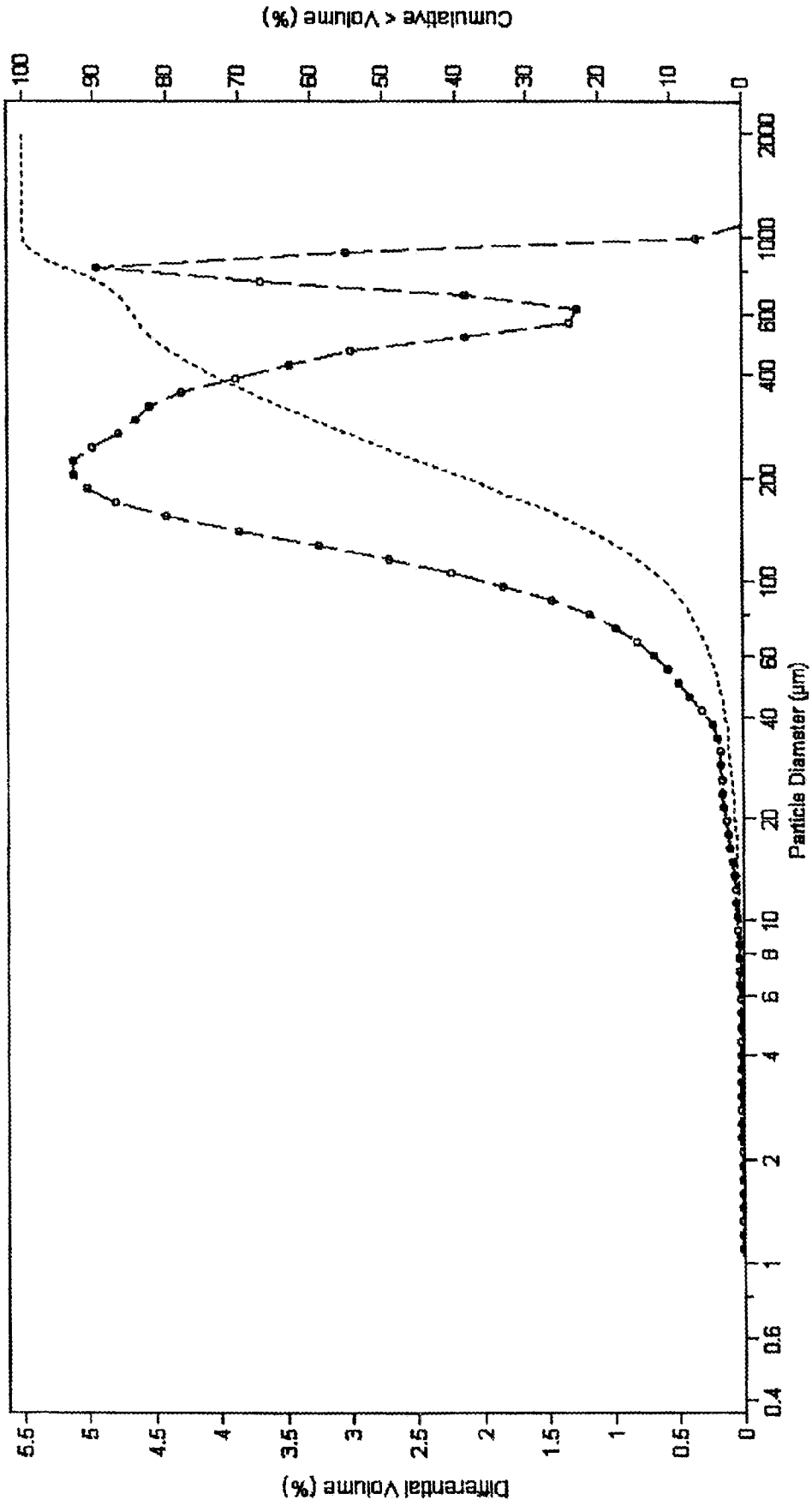
Cumulative < Volume (%)
Differential Volume (%)
Particle Diameter (µm)

Fig. 8

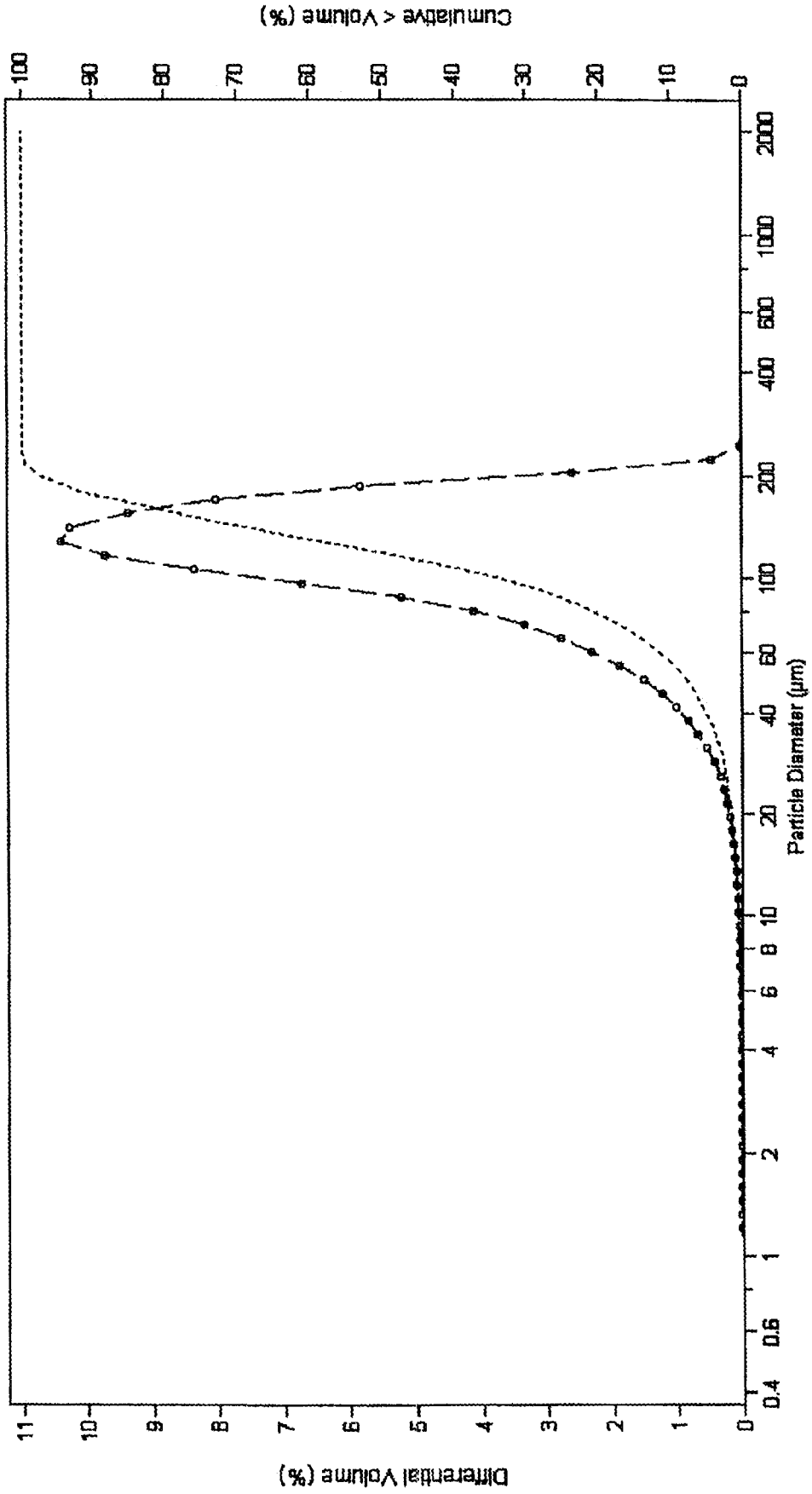
Cumulative < Volume (%)
Differential Volume (%)
Particle Diameter (µm)
0.4
0.6
1
2
4
6
8
10
20
40
60
100
200
400
600
1000
2000

Fig. 9

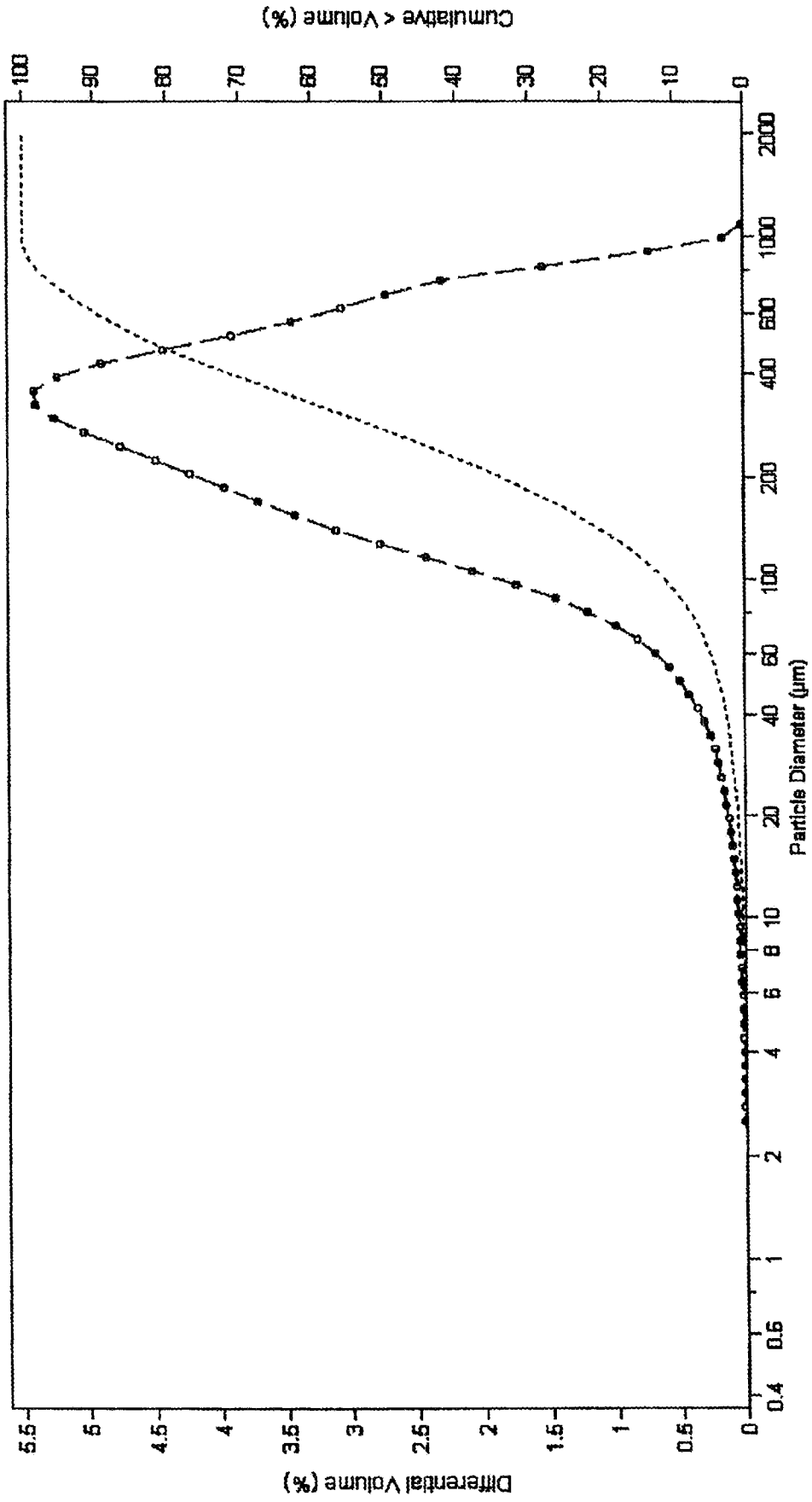
Differential Volume (%)
Cumulative < Volume (%)
Particle Diameter (µm)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
0
10
20
30
40
50
60
70
80
90
100
0.4
0.6
1
2
4
6
8
10
20
40
60
100
200
400
600
1000
2000

Fig. 10

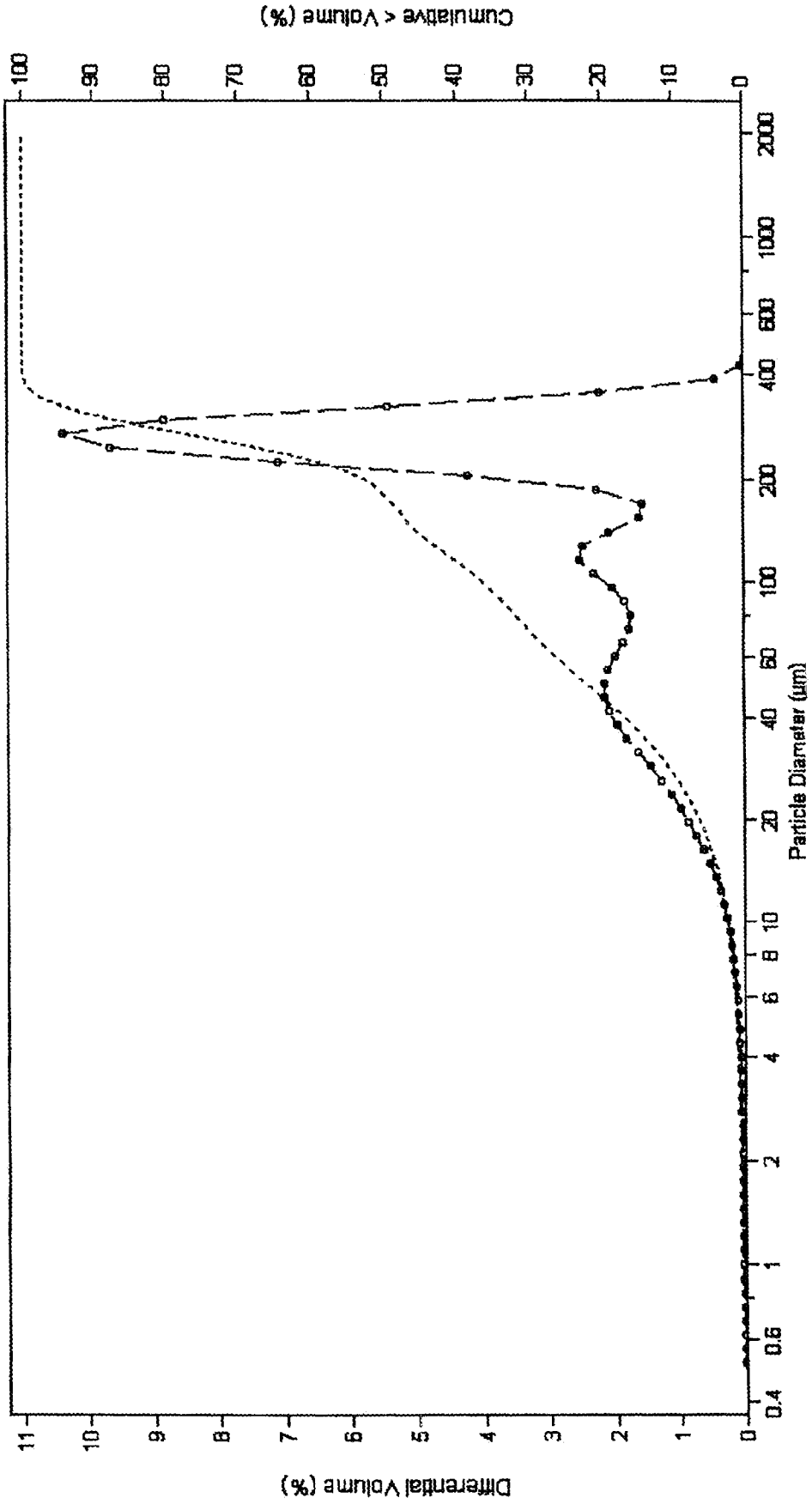
Cumulative < Volume (%)
Differential Volume (%)
Particle Diameter (µm)
0.4
0.6
1
2
4
6
8
10
20
40
60
100
200
400
600
1000
2000

Fig. 11