(54) Title: MANIPULATION OF DISPERSED SYSTEMS

(57) Abstract: The present invention relates to the manipulation of dispersed systems, such as aerosols, smoke, emulsions, suspensions, foams, etc., by application of electromagnetic radiation, such as microwave radiation. The optimal frequency of the electromagnetic radiation is determined by characterising parameters for a dispersed phase in the dispersed systems. The present invention also relates to a method of combining the electromagnetic radiation with an electric field, a magnetic field, an electromagnetic wave (light such as a LASER), and/or a mechanical filter in order to change the dispersed system. The methods are useful for removal of particles from aerosols and smoke. The invention also provides a device which is useful for removal of particles from aerosols/smoke, e.g., emitted from Diesel engines. The present invention further relates to a method for the treatment of heavy-metal containing sewage solution with microwaves.
MANIPULATION OF DISPERSED SYSTEMS

FIELD OF THE INVENTION

The present invention relates to the manipulation of dispersed systems, in particular aerosols/smoke, emulsions, suspensions, foams, etc., in order to facilitate sedimentation/fusion of the phase members of such dispersed systems. In particular, the invention relates to a method for treating aerosol/smoke in order to facilitate separation of particles from said aerosol/smoke.

BACKGROUND OF THE INVENTION

Disperse systems are abundant as a result of a range of industrial processes. In many instances the dispersed systems are highly undesirable and a wide range of means for separation of, e.g., emulsions have been utilised, e.g. by utilising salts, filtration, etc.

Disperse systems are characterised by having a greatly developed interface. One of the phases of a disperse system is generally greatly comminuted and is called the dispersed phase. The latter is distributed in the bulk of a continuous phase called the dispersing medium. The occurrence of disperse systems in nature is very frequent because far from all substances can be dissolved to form molecular solutions, e.g. vesicles and membrane structures of living cells. In modern science and industry, disperse systems play an important role. It is practically impossible to name a branch of industry that does not have to do with disperse (colloid)-chemical processes. These processes are important, for example, in the food industry, the production of rayon, the dyeing of fabrics, the leather industry, agriculture, the science of soils, and naturally in medicine and life science.

The concept of the dispersity characterising the degree of comminution of the dispersed system is commonly used for a general description of the disperse system. The dispersity is expressed in terms of the average diameter of the dispersed phase particles or of the specific surface area of the phase interface. As regards their dispersity, we distinguish coarsely dispersed systems with average particle diameter from 100 to 10.000 nm, and highly dispersed or colloidal systems with an average particle diameter from 1 to 100 nm.

Colloidal systems are also called colloidal solutions. The dispersed phase particles of coarsely dispersed systems can be discerned under a conventional microscope and are retained by a filter paper. Such systems include powders, suspensions, emulsions, foam, and aerosols. This is contrast to colloidal systems, which are not retained by filter paper and are not visibly changed over time.
This being said, formation of dispersed systems causes a number of practical problems in industrial processes. For this reasons, there is a great demand for means of reducing or even eliminating such undesirable dispersed systems.

Many examples of microwave applications in dispersed systems are found in the prior art. However, the important differentiation between this invention and the art is that the examples in the prior art are related to general thermal effects of the dispersed system, whereas the system interactions described in this invention relate to the specific resonance interactions of the components in dispersed systems. Thus, the examples in the prior art are based on general thermal (warm) effects obtained by the radiation whereas this invention relates to parameter specific interactions of a resonance character or in other words this invention relates to "cold" effects on the system.

The application of microwave heating has been used to break emulsions. Fang & Lai reports (Fang, C. S. & Lai, P. M. C., Journal of Microwave Power and Electromagnetic Energy, Vol. 30, No. 1, 1995, 46-56) that by applying microwave radiation to water-in-oil emulsion separation is enhanced, also Chanaa et al. (Chanaa, M. B., Lallamant, M., and Mokhlisse, A., Fuel, Vol. 73, No. 10, 1994, 1643-1649) reports that water/oil emulsions can be separated faster by the application of microwave radiation. The effect it described as an interaction by the radiation at a frequency where the water molecules absorb and thus are heated. No or little absorption of the organic molecules are observed, and thus, the effect is related to the specific heating of water.

Rodriguez-Clemente & Gomes-Morales (Rodriguez-Clemente, R and Gomes-Morales, J., Journal of Crystal Growth 169, 1996, 339-346) reports microwave enhanced precipitation of CaCO₃. It is concluded that the observed effect is based on the specific heating of water and water bound to the micro crystals.

None of these references describes the non-thermal (cold) effects nor are algorithms to compute specific interaction frequencies given.

US 4,582,629 describes the use of microwave radiation in separating emulsions and dispersions of hydrocarbons and water. No dependency between the frequency of the microwave radiation and effect in emulsion separation has been mentioned or substantiated.

SUMMARY OF THE INVENTION

As mentioned above, the undesired formation of dispersed systems in industry often results in extra costs and tedious phase separation processes. Thus, there is a need for
improved or alternative method for phase separation (e.g. phase separation of aerosols/smoke, emulsions, suspension or foams) in the industry, and for separation of particles from smoke from Diesel engines.

5 The present inventors have, as the main aspect of the invention, developed methods, cf. claims 1 and 12, and a device, cf. claim 18, which are very useful for the treatment of disperse systems in order to

The present inventors have, as a second aspect of the invention, also found that

application of electromagnetic radiation of a well-defined frequency and under specific conditions to disperse systems can be utilised in order to manipulate such systems, cf. the method defined in claim 27.

Thus, the present invention in particular relates to a method for manipulating a dispersed system, said dispersed system comprising a dispersing medium and a dispersed phase, said dispersing medium and dispersed phase independently being a solid, a liquid or a gas, and where said dispersed phase is constituted by a plurality of phase members.

The present invention relates to the observation that electromagnetic radiation do interact with the components of dispersed systems (particles, vesicles, bubbles) due to inherent "eigen" modes/frequencies of such components. For, e.g., aerosols/suspensions/emulsions/foams the interaction with the particles/vesicles is due to a resonance effect of the radiation and the particles/vesicles. The resonance interaction for liquids may be either collectively for the whole vesicle or differentially for only a part of the vesicle structure. For solid particles as in, e.g., suspensions/aerosols the interaction is collectively for the particle structure like e.g. the resonance effect known from the interaction between sound waves and crystal glass. Therefore, the specific interaction between a given radiation and a given component of a system is related to system specific parameters.

30 As a third aspect of the invention, the inventors have identified a method for the separation of heavy metal constituents from sewage solutions, cf. claim 33.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 illustrates diffraction patterns for aerosols that are a) non-radiated and b) radiated for 15 min.

35 Figure 2 illustrates the microwave effect on aerosols irradiated for a) for 2 min and b) for 15 min. Notice that the chain shape (clustering) in a) is disappeared in b).
Figure 3a illustrates the electron microscope pictures at different magnification of the same spot of sewage material before microwave treatment. No signals of metals and heavy elements other than the sputtering material, Pt and Si were seen.

Figure 3b illustrates the electron microscope pictures at different magnification of the same spot of sewage material after microwave treatment (2.24 GHz) for 2 minutes at 800 W. Clearly the metals (white areas) have precipitated.

Figure 3c illustrates the EDAX analysis of the chemical composition corresponding to the sample material of Figure 3a.

Figure 3d illustrates the EDAX analysis of the chemical composition corresponding to the sample material of Figure 3b.

Figure 4a illustrates particles from a Diesel combustion engine before microwave treatment.

Figure 4b illustrates particles from a Diesel combustion engine after microwave treatment.

Figure 5 illustrates a device according to one embodiment of the invention. The device includes means of generation of electromagnetic radiation that interacts with particles. The modulation facilitates change of structure and properties of particles. The device also includes means for filtration/sedimentation, e.g. a mechanical filter, an electric field, a magnetic field and/or fotonic filtration. This modulation facilitates removal of particles from the air stream.

**DETAILED DESCRIPTION OF THE INVENTION**

**Dispersed systems**

First of all, it is relevant to note that classification of dispersed systems takes the state of aggregation of the dispersed phase and the dispersing medium into account. Therefore, eight combinations of the states of aggregation of the dispersed phase and the dispersing medium are possible (Table 1).
Table 1: Dispersed systems

<table>
<thead>
<tr>
<th>Dispersing medium</th>
<th>Dispersed phase</th>
<th>Solid</th>
<th>Liquid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid (L)</td>
<td>Colloidal system (sol), Suspension S/L</td>
<td>Emulsion L/L</td>
<td></td>
<td>Foam G/L</td>
</tr>
<tr>
<td>Solid (S)</td>
<td>Alloys, minerals S/S</td>
<td>Solid emulsion, gel L/S</td>
<td></td>
<td>Porous bodies, solid foam G/S</td>
</tr>
<tr>
<td>Gas (G)</td>
<td>Smoke (aerosols), dust (S/G)</td>
<td>Fog, mist (aerosol) L/G</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

Systems with a liquid (L) dispersing medium include: **Lyosols**: a solid body dispersed in the bulk of a liquid (S/L). Examples are colloidal solutions of metals such as gold and silver, and suspensions; **Emulsions**: a liquid dispersed in the bulk of another liquid that does not dissolve in the first one (L/L). Examples are milk, mayonnaise, margarine and “oil”(organic component)/water mixtures; and **Foams**: a gas dispersed in a liquid. (G/L).

Systems with a solid (S) dispersing medium include: **Solid sols**: very minute inclusions of a solid (tiny crystals) dispersed in the bulk of another solid (S/S). Examples are coloured glass, many alloys, and precious stones as ruby and emerald; **Solid emulsions (gels)**: very minute liquid droplets dispersed in the bulk of a solid (L/S). Examples are pearls, opal, silica gel, and alumina gel; and **Solid foams**: a gas contained in the bulk of a solid (G/S). Examples are pumice, tuff, foam concrete, cellular plastics, and foamed glass.

Systems with a gaseous (G) dispersing medium include: **Aerosols**: a solid (S/G) or liquid (L/G) body dispersed in the bulk of a gas. Examples are dust, smoke, fogs, and mists.

It should be noted that also combinations of the above occur in nature called multiphase systems, e.g. a solid + a liquid dispersed in a water or in a gas.

It should be noted that the present invention devices a solution for manipulating, i.e., for most practical reasons, reducing the extent of, or eliminating, dispersed systems based on a liquid dispersing medium, i.e. emulsions, suspensions and foams.

**Origin of disperse systems**

By the principles of thermodynamics, disperse systems cannot be obtained spontaneously. Dispersed systems are usually obtained by the dispersion method in which larger bodies
are physically crushed to smaller bodies. Brittle materials are generally crushed by blows, and viscous ones by attrition. Emulsions are created by vigorous agitation the liquid mixture. Coarsely dispersed systems are prepared in special equipment such as ball mills. Ball mills can produce bodies with diameters down to approx. 1000 nm. Finer commination – to 100 nm and less – is produced in colloidal mills. This equipment is being used to produce water colours, cosmetic powder, drugs etc.

In the condensation method, disperse systems are produced from over-saturated systems. The physical condensation principle is used to describe when a vapour is condensed in a gas phase, e.g. aerosol formation, fog, smoke etc. Also the condensation of a vapour when it passes through a cold liquid (lyosol formation) is a physical condensation, e.g. a sol of metals (Hg, Au, Ag) in water or alkali metals in organic solvents. Chemical condensation is formed in reactions producing sparingly soluble or insoluble compounds, e.g.:

Silver iodide:

15 AgNO₃(sol) + KI(sol) → KNO₃(sol) + AgI(c)

Sulphur:

3Na₂S₂O₃(sol) + H₂SO₄ → 3Na₂SO₄(sol) + H₂O(lq) + 4S(c)

Iron(III) hydroxide:

FeCl₃(sol) + 3H₂O(lq) → 3HCl(sol) Fe(OH)₃(c)

**Kinetic properties**

**Diffusion.** In disperse systems, as in conventional solutions, the particles are in thermal movement. Unlike conventional ones the thermal motion in disperse systems can be observed in a microscope as a chaotic movement of particles, bodies, vesicles, i.e. Brownian motion. The movement will eventually distribute the particles uniformly in the dispersing medium. Consequently, if the content of dispersed particles is higher in different regions, the particles will move from the regions with higher contents to the regions with lower contents. But unlike conventional systems, diffusion in disperse systems proceeds more slowly by one or two orders of magnitude.

**Sedimentation.** A general feature of disperse systems is their kinetic instability, as a result of the dispersed phase particles settle under the effect of a force field i.e. gravitational, centrifugal, electromagnetic, etc, this is called sedimentation. Diffusion counteracts sedimentation but over time the dual effects causes sedimentation-diffusion equilibrium, called sedimentation equilibrium. Sedimentation has great practical significance. For instance, the purification of potable water from suspended particles by sedimentation. It is
also widely used for purifying gaseous production wastes from aerosol particles (dust, soot, moisture). Sedimentation is accelerated by subjecting the gas being purified to the action of an artificial force field produced traditionally in apparatus called cyclones. The same principle in an artificial force field underlies the purification of petroleum and its products of emulsion moisture by centrifugation and be separating cream from milk in separators.

Stability

The stability of disperse systems is a key question when studying their properties. Although disperse systems might resemble conventional solutions (seem to be homogenous, can be transparent, characterised by diffusion and osmosis), disperse systems contradict the laws of thermodynamics because of enormous store of surface energy, which is given away reluctantly. This is called colloidal stability, due to the systems capability to preserve its "homogeneity", e.g. colour, transparency, etc.

Some disperse systems are said to be sedimentation stable if the particles do not settle. This is often found for particles smaller than 1000 nm. When the particles get larger the system will become unstable and sedimentation may occur. However, owing to the tendency of thermodynamic systems to "liberate themselves" from free energy (surface energy) and the particles in the systems tend to consolidate by sticking together. This leads to disturbance of the sedimentation stability.

Systems with constant particle size are called aggregation stable. This also affects the sedimentation stability of the systems and is therefore an important determinant for the future fate of a system. A reduction in dispersity (consolidation) is called coagulation.

Coagulation is promoted by adsorption forces "observing" the principle of free surface energy, but is counteracted by electrostatic forces of repulsion acting between particles of same electric charge.

The coagulation effect of electrolytes is of major importance in the petrochemical industry.

For example, salting out is the main technique to remove emulsion water from petroleum and also when separating rubber from latex's.

The influence of the temperature on disperse systems is dual: elevation of temperature increases the Brownian motions, which increases sedimentation stability, but on the other hand it weakens the adsorption of ions/medium molecules which "strips" the aggregate nucleus thus facilitating aggregation. Therefore, disperse systems retain their properties up to a certain temperature (critical temperature), which might be above 100 degrees.
Therefore is does moderate temperature changes not affect disperse systems. The critical temperature is highly system dependent and therefore different from system to system.

Surfactants are known to adhere to the dispersed particle and thereby reduce the surface energy. This increased thermodynamic stability stabilizes the dispersed system. Such systems can acquire such high stability that they form spontaneously, e.g. instant coffee, which is composed by coffee powder and a surfactant, collargol.

Emulsions

Emulsions are disperse systems formed by two immiscible liquids one of which is dispersed in the bulk of the other. The particle size of the dispersed phase in emulsions varies within broad limits from the colloidal region (100-1,000 nm) to the coarse region in which the droplets can be seen under microscope. Emulsions relate either to the oil-in-water type (O/W – emulsions of the first order, e.g. milk, sweet cream, etc) or to the water-in-oil type (W/O – emulsions of the second order, e.g. margarine, mayonass, butter, etc.).

Emulsions can be prepared by the presence of emulsifiers, by mixing, in colloidal mills, and by ultrasound. The best emulsifiers are surfactants which exhibit a hydrophilic-lipophilic balance i.e. having identical affinity for water and an organic solvent. Examples are the alkali salts of aliphatic saturated fatty acids of chain length of 12 to 18 carbon.

In dilute emulsions, the total volume of the dispersed phase does not exceed 0.1 % of the total volume of the system. They are generally colloidal solutions with all the relevant properties: sedimentation stability, exhibit Brownian motion, electro-osmosis, etc.

In concentrated emulsions the total volume of the dispersed phase does not exceed 74% of the total volume of the system. They are generally coarsely dispersed systems. They easily form droplets of the dispersed phase, i.e. coalesce. Emulsions are considered to be highly concentrated when the volume exceeds 74% of the total volume of the system. The particles are often irregular polyhedrons. These systems tend to phase invert and new dispersed dispersing phase forms.

Destroying emulsions is also very important. The traditional procedures are by salting out, the use of strong mineral acids, centrifugation. For example a latex polymer is separated by salting out, petroleum and its products is dehydrated by an electric field; butter is separated from milk by centrifugation; and in preparative chemistry organic substances are separated from water by salting out or by demulsifiers.

Emulsions are easily formed during extraction processes and constitute a major problem in industrial preparative chemistry. But a single efficient method is presently not available. Again either demulsifiers are used or the methods described above.
Foams

Disperse systems in which a gas is the dispersed phase and a liquid is the dispersing medium is called liquid foams, while those with a gaseous dispersing medium are called solid foams. Dilute liquid foams are kinetically unstable and therefore concentrated foams are of most practical importance.

Foams are coarsely dispersed systems. The gas bubbles in them are large in size (they can be seen by the naked eye). They are firmly pressed against each other and are separated only by thin inter-layers of the dispersing medium – a foam film.

Foams are produced by dispersion methods such as forcing the gases through narrow orifices or by intensive agitation of the liquid in the presence of the gas. Foams can also be produced by condensation methods as a result of formation of gaseous products, e.g. rising by decomposition of bicarbonates, rising by yeast growth.

Foams have diverse applications: used to concentrate materials by flotation, in laundering and washing, in fire extinguishing, used in insulation materials (foam concrete-glass), in the production of plastic foams (flexible PVC, polystyrene, polyester, etc).

Foam formation can also be problematic in various applications: when foam formation is not tolerated during mixing, distillation, evaporation, or similar operations. In particular foam formation is problematic in treatments of effluent waters, e.g. foams in sewage can cover the surface and thereby kill the flora and fauna. Traditionally foams are destroyed by adding surfactants but also other organic compounds have been used as thermal and mechanical methods.

Aerosols

Aerosols are dispersed systems in which liquid or solid (crystalline) particles of the dispersed phase are distributed in the volume of a gas. The size of the dispersed phase particles in aerosols varies within broad limits, from 50 to 10,000 nm, including the region of colloidal and coarsely dispersed systems. Two types of aerosols are distinguished, namely, a liquid in a gas – L/G (mists), and a solid in a gas – S/G (dust, smoke).

Aerosols are produced by condensation and dispersion methods, e.g. condensation of water in air constitutes mists and incomplete combustion of fossil material produces smoke. Aerosols can also be produced chemically, e.g. by reacting ammonia with hydrochloric acid, or of sulphur trioxide and water vapours. The condensation method produces aerosols during mechanic agitating, dust produced during industrial processes, in blasting and agricultural work, when grinding cement clinker, in the production of cement,
and in grinding cement. Aerosols are also employed in medicine or for controlling agricultural pests.

Aerosols are aggregately unstable, but owing to the features of the gaseous dispersing medium, they have a high sedimentation stability. Aerosols are similar to solutions in a number of properties: thermodynamic instability, Brownian motions, diffusion, sedimentation, the Tyndall effect, electrophoresis, etc. But the gaseous dispersing medium introduces some novel features: light scattering is much greater than in colloidal solutions, Brownian motion and diffusion is more intensive, the electric charge of the dispersed particles is negligibly.

Specific properties are thermophoresis and photophoresis. Thermophoresis is based on the fact the dispersed particles are moving away from heated surfaces and the fact that the particles have a tendency to settle on cold surfaces. Photophoresis is another property used to describe that the particles are either moving towards or away from light sources.

Prevention of aerosols is very important. Examples are removing dust from air which has tremendous applications e.g. in mines, mill, tyre plants, removing dust particles from diesel cars, removing tobacco smoke in air cleaning, removing dust from chimneys, etc. Traditionally this has been done by applying filters on which the particles settle, artificial force fields, and in cyclones where the particles are thrown via centrifugal forces on the walls of the cyclone. Electrical filters employing a strong electric field have also been used to settle particles. This method however, requires that the particles are charged.

Suspensions

Suspensions are disperse systems with a liquid dispersing medium and a solid dispersed phase. They differ from colloidal solutions in a larger particle size (>1000 nm). Depending on the relative content of the dispersed phase, suspensions are divided into three types: dilute, concentrated, and highly concentrated. The latter are usually called pastes. Owing to the large size of the dispersed phase particles, Brownian motion is absent in suspensions. Consequently, no diffusion occurs in them and no kinetic properties associated with diffusion (osmosis, sedimentation equilibrium) are observed in them. Aggregative and sedimentation instability is a characteristic feature of suspensions. A significant property of suspensions is their structuring, which consists in the formation from the dispersed phase particles of a spatial network whose loops accommodate the dispersing medium. Structuring is explained by van der Waals or electrostatic interactions between the dispersed phase particles. In concentrated suspensions, this can result in a gel, which structure can be destroyed by agitation. This is a reversible process called thixotropy. Thixotropy is of major importance in industry, e.g. in drilling petroleum wells.
special additives are added to the wash water to prevent gel formation, and paints must also be thixotropic i.e. remain fluid when applied and rapidly set after painting.

The present invention comprises the general observation that the properties of dispersed systems can be changed or manipulated by electromagnetic radiation. The interaction is system specific and by applying system parameters a specific frequency of the given system at a given state can be calculated. The interaction will change with the present state of the system or the equilibrium of the system. For instance a system in a steady state (e.g. colloidal system) can be induced to aggregate by the manipulation, or an aggregating system can be induced to form a stable more or less mono-dispersed system. The fate of the manipulation, fusion or fission of particles-vesicles/bubbles is dependent on the state of the system and the radiation frequency of the electromagnetic radiation.

An example of the fission process is when growing crystals in solution at a certain state/frequency situation is becoming resonant with the radiation and accordingly are divided into smaller particles, comminuted. This process can form a stable colloidal system. An example of the fusion process is when vesicles in an emulsion of any composition in a given state/frequency situation is becoming resonant with the radiation and accordingly opens and fuses to larger vesicles.

The methods and the device according to the first aspect of the invention

It is a key observation of this invention that electromagnetic radiation can interact with a dispersed phase by changing the physical state, i.e. size, composition, structure, etc. after which it is possible to change and modulate the system. It is also comprised in this invention that electromagnetic radiation can interact with the elements of dispersed systems and thereby changing the electric and magnetic properties of the components. Thus, the electromagnetic radiation will change the initial, primary, state of the system to a secondary state. The degree and nature of the secondary state of the individual components of the system will depend on the physical nature of the systems. Thus, it is anticipated that some systems will have strongly induced secondary effects whereas other systems will have smaller or no secondary effects.

It is also an important part of this invention to manipulate disperse systems by electromagnetic radiation, called the primary manipulator, in combination with a secondary manipulator. Said secondary manipulator is an additional physical modulator of the dispersed system that is capable to interact with the secondary state of the system. It is known that electromagnetic radiation can interact with metals and induce secondary effects, e.g. spark generation of metals in a microwave oven. It is therefore part of this invention that induced changes by the radiation can be utilized by a secondary manipulator
to change the system further. In the case where the electric/magnetic properties of a particular component of a system is changed, a corresponding electric/magnetic field and/or electromagnetic wave (light) can be used to manipulate the system, i.e. a secondary manipulator. E.g. in the case where the electromagnetic radiation has changed or induced an electric charge or a magnetic field of the particles, a corresponding electric/magnetic field and/or an electromagnetic wave (light) can be used to sediment the particles. For instance, in a smoke generator, i.e. a diesel engine, the particles may first be manipulated with electromagnetic radiation and then subsequently be manipulated by an electric/magnetic field and/or an electromagnetic wave (light). That field or wave will remove the particles by strongly increasing the sedimentation speed. The electromagnetic wave comprised in this invention may be a LASER. It is an advantage to use LASERS in this context due to the very high intensity of the light.

Thus more specifically, the invention provides a method for manipulating a dispersed system, said dispersed system comprising a dispersing medium and a dispersed phase, said dispersing medium and dispersed phase independently being a solid, a liquid or a gas, where said dispersed phase is constituted by a plurality of phase members, the method comprises the step of treating the dispersed system with a primary manipulator in the form of electromagnetic radiation in order the change the properties of the phase members, and subsequently treating the dispersed system with a secondary manipulator in order to facilitate sedimentation/fusion of the phase members.

In one embodiment, the electromagnetic radiation (the primary manipulator) is applied as defined in under "the second aspect of the invention".

The electromagnetic radiation (the primary manipulator) typically has a frequency in the range of 0.001-1000 GHz, preferably in the range of 0.01-100 GHz, and as mentioned before, the frequency may be determined according to the "second aspect of the invention".

It will also be understood that the secondary manipulator plays an important role for this method of the invention, i.e. the secondary manipulator may be (i) an electric field of in the range of $1.0 \times 10^5$ V, such as in the range of $100-10^4$ V, or (ii) a magnetic field of in the range of $10^4-10^3$ Tesla, such as in the range of $10^5-10^3$ Tesla, or (iii) an electromagnetic wave (light) of a wavelength in the range of 10-10,000 nm. In the latter case, the electromagnetic wave is preferably a LASER.

The advantage of the method described here is that it is possible to remove solid particles in smoke in a "non-invasive" manner. It is a particular problem to remove the very fine
particles from smoke generators, e.g. Diesel engines, because the traditional smoke removers, filters, have to be very fine. Fine filters are difficult to use because they essentially “clot” the exhaust system whereby significant energy is lost.

Thus, in one particularly relevant embodiment, the dispersed system is an aerosol/smoke where the dispersing medium is a gas and the dispersed phase is a solid (particles).

Subsequent to treatment of the aerosol/smoke with the first manipulator and the second manipulator, the particles of the aerosols/smoke (typically in partly fused or sedimented form) may advantageously be subjected to a filtration step in order to remove at least a portion of said particles from said gas.

In one variant, the filtration is performed by a mechanical filter, e.g. a finely meshed filter unit with the capability to withhold particles.

In another variant, the filtration is performed by an electromagnetic wave, in particular a LASER.

An alternative method of this aspect of the invention is also provides, namely a method for manipulating a dispersed system, said dispersed system comprising a dispersing medium and a dispersed phase, said dispersing medium being a gas and said dispersed phase being a solid, where said dispersed phase is constituted by a plurality of phase members (particles), the method comprises the step of treating the dispersed system (an aerosol) with a primary manipulator in the form of electromagnetic radiation in order to change the properties of the particles in order to facilitate sedimentation/fusion of said particles so that the particles can subsequently be removed from the dispersing medium (the gas).

As above, in one embodiment, the electromagnetic radiation (the primary manipulator) is applied as defined in under “the second aspect of the invention”.

Also as above, the electromagnetic radiation (the primary manipulator) typically has a frequency is in the range of 0.001-1000 GHz, preferably in the range of 0.01-100 GHz, and as mentioned before, the frequency may be determined according to the “second aspect of the invention”.

Subsequent to treatment of the aerosol/smoke with the first manipulator, the particles of the aerosols/smoke (typically in partly fused or sedimented form) may advantageously be subjected to a filtration step in order to remove at least a portion of said particles from said gas. In one variant, the filtration is performed by a mechanical filter, e.g. a finely
meshed filter unit with the capability to withhold particles. In another variant, the filtration is performed by an electromagnetic wave, in particular a LASER.

The invention also provides a device which is useful for removal of particles from smoke.

Thus, the invention provides a device for removal of particles from aerosols/smoke in a continuous manner, said device comprising a conduit for passage of the particles of said aerosol/smoke, and means for application of electromagnetic radiation to said particle upon passage of said conduit.

In one embodiment, the device further comprises means for application of an electric field of in the range of 1.0-10^6 V, such as in the range of 100-10^4 V, to said conduit.

In another embodiment, the device further comprises means for application of a magnetic field of in the range of 10^-5-10^-2 Tesla, such as in the range of 10^-5-10^-3 Tesla, to said conduit.

In a still further embodiment, the device further comprises means for application of an electromagnetic wave of a wavelength in the range of 10-10,000 nm to said conduit. The electromagnetic wave is preferably a LASER.

Most preferably, the device also further comprises means for mechanical filtration.

In a particularly interesting embodiment, the device comprises means for application of an electric field of in the range of 1.0-10^6 V and/or means for application of a magnetic field of in the range of 10^-6-10^-2 Tesla in combination with means for application of an electromagnetic wave (light) of a wavelength in the range of 10-10,000 nm. Furthermore, the device may comprise means for mechanical filtration.

It is anticipated that such devices can be mounted in connection to a combustion engine. Depending on the size of the engine, the devices will have different size. Thus, small devices will be used on e.g. cars and larger devices will be used on e.g. trucks and ship engines. Such devices may comprise a first manipulator applying an electromagnetic radiation to the aerosols/smoke. Said first manipulator may be sufficient to sediment the particles or to increase the size of the particles so traditional filtration is easy to perform. Thus, the sedimentation device may comprise the primary manipulator in combination with and actual particle removing unit. This unit may be a traditional filtration unit, a filter, or preferred a "non-invasive" filter in the form of an electromagnetic wave. A preferred electromagnetic wave is a LASER.
Said primary manipulator can also be connected to a secondary manipulator applying an electric/magnetic field and an electromagnetic wave (light) to the aerosols/smoke. The collective actions will rapidly settle the particles. It is anticipated that an effective particle removing device will contain both the primary and the secondary manipulator. Such a “dual” manipulating device will increase the sedimentation speed of the particles so that the particles are easy to remove. The actual particle removing step may be a combination of applying an electric/magnetic field to the particles in combination with an electromagnetic wave. In the systems where electromagnetic waves are needed, it will be a preferred embodiment to use a LASER. It is also anticipated the actual particle removing unit may be a traditional smoke filtration unit, however, it is a preferred embodiment to use a “non-invasive” filtration, such as the electric/magnetic field and/or the LASER.

Said device can be mounted on the exhaust systems on regular e.g. cars/trucks/ship engines/power plants or other smoke generating things and remove the particles of the aerosols, smoke, generated during the combustion. It is a straightforward technology to actual combine an electromagnetic radiation source, e.g. a magnetron, with the electric/magnetic generators and/or the LASER in one unit. These components will be mounted around the pipes of the aerosol generator, e.g. the Diesel engine.

This being said, the invention also provides an exhaust system of a combustion engine which comprises a device as defined hereinabove. The combustion engine is preferably a Diesel engine.

In the case of sewage treatment, electromagnetic fields can enhance precipitation of heavy metals as demonstrated in the examples shown below. A further secondary manipulation of applying a magnetic/electric field can extract the heavy metals, usually being harmful, from the less harmful rest. (See also the “third aspect of the invention”.)

The method according to the second aspect of the invention

As mentioned above, disperse systems are characterised by having a greatly developed interface. One of the phases of a disperse system is generally greatly comminuted and is called the dispersed phase. The latter is distributed in the bulk of a continuous phase called the dispersing medium.

The dispersed phase will in the present context be considered as being constituted by a plurality of phase members. Such phase members may, when the dispersed phase is a solid be particles or, when the dispersed phase is a liquid, be vesicles.
Based on new knowledge, the present inventors have found that dispersed systems can be considered as systems that are not in an equilibrium state, and that such equilibrium state typically is a phase-separated state. It is also observed that an equilibrium state exists for dispersed system, but that substantial equilibration without external intervention in certain instances may require extreme periods of time. Thus, the present inventors have now found that application of electromagnetic radiation, which has a frequency that specifically relates to characterising parameters for the dispersed phase of the dispersed system can facilitate the equilibration of a dispersed system (thereby in certain instances breaking up (phase separating) the dispersed system).

Thus, the present invention provides a method for manipulating a dispersed system, said dispersed system comprising a dispersing medium and a dispersed phase, said dispersing medium and dispersed phase independently being a solid, a liquid or a gas, where said dispersed phase is constituted by a plurality of phase members, where the method comprising applying electromagnetic radiation having a frequency corresponding to the estimated average excitation frequency, \( v \), for the phase members.

By the term "corresponding to the estimated average excitation frequency" is meant that the frequency of the applied electromagnetic radiation is able to excite at least some of the phase members having in mind that the phase members may represent a certain size distribution, i.e. the phase members are for practical reasons never completely monodispersed. Thus, the frequency could be slightly off the "optimal" (central) excitation frequency without a detrimental influence on the effect. The frequency of the applied electromagnetic radiation is typically in the range of \( 1/12 \) to 12 times the average excitation frequency for the phase members. Preferably, the frequency of the electromagnetic radiation is in the range of \( 1/8 \) to 8, such as \( 1/5 \) to 5, e.g. \( 1/2 \) to 4, times the estimated average excitation frequency.

By "average" is meant that the excitation frequency in question should be based on the number average for the radius of the phase members of the system. In particular, when the system is containing, e.g. particles, in many different sizes a broader spectrum frequencies is needed. If the system is monodisperse essentially one optimal average frequency can be used.

When turning to the estimation of average excitation frequency, it has been found that the characterising parameters of the dispersed system can be reduced to parameters relating to the size of the phase members and to a few material parameters. Thus, when the dispersing medium is a liquid and the dispersed phase is a liquid (emulsion), the phase members are in the form of vesicles (surrounded by the dispersing medium), such vesicles
are initially characterised by the radius (r) of the vesicles, the surface tension (γ) of the vesicles and the density (ρ) of the material constituting the vesicles. Alternatively, when the dispersing medium is a liquid and the dispersed phase is a solid (suspension), the phase members are in the form of particles (surrounded by the dispersing medium), such particles are initially characterised by the radius (r) of the particles, the Young's modulus (E) of the particles and the density (ρ) of the material constituting the particles. Also alternatively, when the dispersing medium is a liquid and the dispersed phase is a gas (foam), the phase members are in the form of gas bubbles (surrounded by the dispersing medium), such bubbles initially being characterised by the radius (r) of the bubbles, the surface tension (γ) of the bubbles, the density (ρ) of the material constituting the bubbles, and the difference (Δp) between the inner and the outer pressure of the bubbles;

Similar parameters can, as will be appreciated by the person skilled in the art, be considered for the other possible dispersed systems mentioned in the introduction.

With respect to the estimated average excitation frequency for a dispersed system where the dispersing medium is a liquid and the dispersed phase is liquid, it has been found that electromagnetic radiation can induce an elongation motion of stretch modes in the of the vesicles which will facilitate the fusion of vesicles. Thus, when the dispersing medium and the dispersed phase are both liquids, the average excitation frequency, ν, for the vesicles of the dispersed system before application of electromagnetic radiation is estimated by the following formula I

\[ \nu = \frac{1}{\pi} \times \sqrt{\frac{5 \times \gamma}{6 \times \pi^3 \times \rho}}. \]

As an example, the estimated average excitation frequency for a oil-in-water emulsion comprising water and n-octylalcohol, where the number average radius of the vesicles is 1.0 μm, the density of the n-octylalcohol vesicles (phase members) is 0.85 g/cm³, the surface tension is 0.85 N/m (850 dyne/cm) can then be calculated as:

\[ \nu = \frac{1}{\pi} \times \sqrt{\frac{5 \times 0.85}{6 \times \pi^3 \times 0.95 \times 10^{-3}}} = 8.7 \text{ GHz} \]

A similar estimation can be set up for other dispersed systems, thus, when the dispersing medium is a liquid and actually also air and the dispersed phase is a solid (suspension, aerosols), the average excitation frequency, ν, for the particles of the dispersed system before application of electromagnetic radiation is estimated by the following formula II

\[ \nu = \frac{1}{\pi \times r} \times \sqrt{E \times r / \rho} \]
A further estimation can be set up for a dispersed system where the dispersing medium is a liquid and the dispersed phase is a gas (foam), the average excitation frequency, \( v \), for the particles of the dispersed system before application of electromagnetic radiation is estimated by the following formula III:

\[
v = \frac{1}{\pi} \times \sqrt{\left(\frac{5 \times (\gamma + \Delta \rho \times r)}{(6 \times r^3 \times \rho)}\right)}
\]

One of the advantages by the present invention is the accuracy by which the electromagnetic radiation can be applied to a dispersed system. Also, in the events where the thermal effects and other side effects of forced phase separation should be avoided, the present method is superior over known methods in the field of phase separation. This is particularly true where a temperature raise is undesirable or even prohibitive in view of the subsequent use of the components constituting the dispersed system.

Preferably, the frequency of the electromagnetic radiation is in the range of 1/8 to 8, such as 1/5 to 5, preferably 1/2 to 4, times the estimated average excitation frequency.

According to a particular aspect of the invention, the electromagnetic radiation is applied in such a manner and under conditions that any temperature increase for the dispersed system is at the most 20 K, such as at the most 10 K, e.g. at the most 5 K, in particular at the most 3 K, e.g. at the most 1 K, or such that essentially no increase in temperature is obtained.

When found desirable, the dispersed system can be temperature regulated, e.g. thermostated to a predetermined temperature, during at least a part of the period of application of electromagnetic radiation.

Also, due to the well-controlled conditions under which the manipulation of the dispersed system (in particular emulsions) is conducted, it is highly realistic that the conditions can be controlled so that the duration of the application of electromagnetic radiation is so that the average vesicle/particle/bubble radius is between 1.1 to 10 times, such as 1.2 to 5 times, preferably 1.3 to 3 times, of the initial vesicle/particle/bubble radius.

With respect to the duration of the electromagnetic radiation, it is believed that the application should preferably not be continued when the average excitation frequency of the system (after application of electromagnetic radiation) falls outside the range of 1/12 to 12 times the frequency of the applied electromagnetic radiation.
Although it is envisaged that increase in the vesicle (or particle or bubble) radius will lead to a rapid phase separation, it is also contemplated within the present invention that the frequency of the electromagnetic radiation may be gradually lowered corresponding to the increase in the vesicle (or particle or bubble) size and thereby decrease in average excitation frequency.

Thus, in a particular embodiment, the frequency of the electromagnetic radiation is at any time in the range of 1/12 to 12 times the existing estimated average excitation frequency. Preferably, the frequency of the electromagnetic radiation is at any time in the range of 1/8 to 8, such as 1/5 to 5, e.g. 1/2 to 4, times the existing estimated average excitation frequency.

In some embodiments, more than one average frequency is determined for disperse systems containing particles-vesicles of different sizes, i.e. the electromagnetic radiation is applied at two or more frequencies.

The duration of the application of electromagnetic radiation will of course depend on the applied power and the dispersed system in question. It is generally believed that application of electromagnetic radiation (either continuously or periodically) can be conducted within 10-1000 sec, e.g. within 10-100 sec.

The effect applied should preferably be in the range of 0.1-1000 W per kg of dispersed system/material. Preferentially 1-100 W per kg of dispersed material.

**Microwave apparatus**

In many instances, a magnetron has been used for electromagnetic radiation (microwaves at 2.24 GHz). Microwave radiation at other frequencies was generated by specially build microwave cavitatations. In order to allow the frequency to vary according to the decrease in vesicle/particle/bubble size, variable frequency apparatuses should be used.

For detection of the initial vesicle or particle or bubble size, and for monitoring the progress of the decrease in size, scanning electron microscope with EDAX, ORD (optical rotational dispersion), X-ray diffraction attached to TEM, and general chemistry small lab equipment can be used.

**The method according to the third aspect of the invention**

A particular aspect of the invention is the treatment of heavy-metal containing sewage solutions in order to facilitate isolation of said heavy metal constituents in solid form. Example 9 illustrates this method.
More generally, the present invention also provides a method for the separation of heavy metal constituents from sewage solutions, said method comprising

5 a) obtaining a sewage solution,
b) applying microwaves to said solution, and
c) isolating the heavy-metal enriched precipitate from said microwave treated sewage solution.

10 It should be understood that the sewage sample may be pretreated, e.g. by dilution, concentration, and/or addition of chemicals. It should also be understood that the invention may be generally applicable for waste water solutions in general.

15 The frequency of the applied electromagnetic radiation is in the range of 0.001-1000 GHz, in particular in the range of 0.01-100 GHz, and more typically the frequency of the applied microwaves is typically in the range of 0.1-10 GHz, in particular in the range of 0.5-5 GHz. Thus, a standard magnetron can often be used.

20 In a particular embodiment of this aspect of the invention, the treatment of the sewage solution is conducted in a continuous manner, e.g. an integrated treatment step in a waste water treatment plant.

THEORETICAL SECTION

25 Introduction

The following section contains investigations on what we call colloidal or dispersed systems, especially with respect to radiation effects. These colloidal systems are basically divided into suspensions (e.g. salt in solution), emulsions (e.g. oil/water mixtures) and aerosols (e.g. micro-particles in air). We shall show that these systems can be influenced, with respect to particle distribution, phase, solubility, etc, by electromagnetic radiation.

It is well known, that there are classical mixtures of liquids that are very difficult to separate in phases. The problems with mixtures that are difficult to separate occur often in the case of oil/water mixtures in waste situations and it will be of great importance if the separation process can be speeded up by non-invasive means, as we shall demonstrate. In a theoretical treatment of phase separation, hydrophobic problems are often treated. In
this the substance, to be dissolved, has formed small vesicles that are difficult to break up and which prevent fusion of the vesicles. In the precipitation of colloidal substances, fusion as well as fission will be discussed.

5 There have been several articles appearing in the literature recently that have reported on success in applying electromagnetic radiation on the problem of separating oil from water. The radiation has mostly been in the frequency range of a standard magnetron microwave appliances, and the microwave effects are often explained in terms of thermal phenomena. Here, we will give evidence for a non-thermal component of the microwave effects that is the dominant effect.

Theory

In a theoretical treatment of the problem of phase separation of emulsions, the problem can - according to the understanding of the present inventors - in many instances be dealt with as a hydrophobic problem where the substance to dilute has formed small vesicles that are difficult to break up and which cause prevention of fusion among the vesicles. This problem of vesicles does not only apply to emulsions but also to other dispersed systems where similar considerations can be applied. Thus, the problems of phase separation can generally be considered as problems of fusion as well as fission.

20 In the following, we estimate the frequency that the applied radiation for getting an optimal effect on the three main classes of systems, i.e. emulsion, suspension, and aerosols.

Let us first try to estimate the possible frequency of applied electromagnetic radiations that yield to fusion of two vesicles in the case of an emulsion of a hydrophobic liquid in water. We claim that we can induce an elongation motion of stretch modes of these vesicles by electromagnetic radiations that facilitate their fusion. Take vesicles of an oil. They have during stretch modes a conservation of volume but instability modes driven by curvature. The potential energy (E) for a vesicle deformed by the parameter η can be written, in a harmonic approximation, as

\[ E_{\text{pot}} = \frac{1}{2}K\sigma^2 \]

With the coefficient K being calculated from the analysis of increased surface times surface tension for spherical vesicles it is given in terms of the surface tension γ:

\[ K = (5/6)\gamma \]
Next, we can write the kinetic energy ($E_{\text{kin}}$) in terms of an effective mass $m$ that is the part of the whole mass of the vesicle that is moving,

$$E_{\text{kin}} = \frac{1}{2}m \left( \frac{d\alpha}{dt} \right)^2$$

The equation of motion is seen to be satisfied by the wave solution $\phi(\xi - \omega t)$ and the characteristic “resonance” frequency is the function,

$$\nu = \frac{1}{(\pi) \times \sqrt{K/m}} \quad \text{or}$$

$$\nu = \frac{1}{\pi} \times \sqrt{\frac{5\gamma/6 \times r^3 \times \rho}{}}$$

where $K$ is the Force constant (Young module $E$), $r$ is the radius of the vesicles, $\gamma$ the surface tension and $\rho$ is the density. In the case of $r = 1 \mu$m and $K = 0.070 \text{ N/m}$ (70 dyne/cm) and $\rho = 1 \text{ g/cm}^3$ then $\nu$ is approx. $10^9 \text{ Hz}$.

For oil/water emulsions, we get explicitly the formula $\nu = \frac{1}{\pi} \times \sqrt{\frac{5\gamma/6 \times r^3 \times \rho}{}}$.

For suspensions/aerosols, we have generally

$$\nu = \frac{1}{(\pi) \times \sqrt{K/m}} = \frac{1}{(\pi \times r)} \times \sqrt{E \times r / \rho}$$

while the foam/bubble system also involves a pressure difference $\Delta p$ so the frequency formula becomes:

$$\nu = \frac{1}{\pi} \times \sqrt{5 \times \frac{(\gamma - \Delta p \times r)}{(6 \times r^3 \times \rho)}}$$

where $\Delta p$ is the pressure difference between the inner and the outer pressure of the bubbles. The reason for their appearance in the formula is that equilibrium for the bubbles is $\gamma = \Delta p \times r$.

When the dispersed medium is a liquid there will be a damping effect.

For aerosols, the solid phase is expected to have somewhat different Young modules (e.g. for carbon particles $E = 1.26 \text{ Kg/m}^2$ and surface tension gamma = $0.0126 \text{ N/m}$) which means that the frequency is in the same range as suspension.

We have given here an example of the process of fusion of oil drops by a jiggling stretch mode. The same process can also be applied to precipitation in suspensions. We have
chosen the example of precipitation of a platinum suspension that is known to be hard to agglomerate. Colloidal particles of platinum will agglomerate much faster under the influence of electromagnetic radiation in the microwave range. Since the surface tension is of another range than that of oil drops and so is the size of the platinum particles compared to that of the oil drops we still see a sizable (visible) effect at the same microwave frequency. Since the same formula is assumed to apply for the two mentioned cases, it is reasonable to explain the coincidence by the fact that the increase in the size has been balanced by an increase in the surface tension.

The phenomena of solubility, thought to occur under the process of fission, can as well be explained by the same formula where particles are cracking or splitting again by stretch modes, as it is expected for the equilibrium state. Hence, according to our theory, we can expect that the application of electromagnetic radiation will enhance the process towards equilibrium such that if the equilibrium involves brake-up of particles the relevant mechanism is that of fission, while the agglomeration leading to the equilibrium state involves fusion of particles.

EXAMPLES

A standard domestic microwave oven operating at a frequency of 2.24 GHz has been used in most of the following experiments although it would have been desirable to use a source with a variable frequency emission. Although the frequency of the microwave oven in some instances was outside the required range of 1/12 to 12 times the estimated average excitation frequency, the effects (although far from optimal) were believed to be seen due to the fact that a measurable amount of the vesicles/particles/bubbles had a size corresponding to the applied frequency, i.e. the heterogeneous systems (emulsions, aerosols, and suspensions) with a fairly broad distribution of vesicle/particle size.

In the case of more practical application of this technology, one would preferably work with specifically adapted equipment providing the desired frequency, or with a source of electromagnetic radiation with a variable frequency, or with a frequency different from the domestic microwave oven.

All chemicals were reagent grade and from Sigma/Aldrich and Fluka. The microwave oven was a 600 W domestic microwave oven operating at a frequency of 2.24 GHz.

All experiments concerning disruption of emulsions were performed essentially in the same way. The first experiment (Examples 1-2) will be described in detail and in the following experiments (Examples 3–6) only the differentiation factors from the first experiment will be described.
Emulsions

The most well known emulsions are oil-water mixtures, where the oil is salad oil. In the experiments described below, a domestic microwave oven with a fixed frequency emission was used. For all the irradiated samples, fast separation of the phases was seen, also for the ethanol/paraffin oil emulsion. The temperature was typically allowed raised from 22-24 °C to 42-45 °C. Control samples produced in exactly the same way as the irradiated ones were placed in a 50 °C water bath. The irradiated samples were separated during the irradiation time (15-45 seconds), whereas the non-irradiated samples were only partially separated even after several hours.

When cyclohexylchloride is synthesised (see Example 2), it produces a very dense emulsion. It usually takes a couple of days to give complete separation of this emulsion by means of an ordinary separation funnels and gravity, but microwave radiation treatment (in a domestic microwave oven) enhanced the separation rate with a factor 1/20. The frequency of radiation in a similar experiments (not described) was varied from 1 GHz to 3 GHz in a designed 500 mW reactor. It was found that the optimal frequency was close to 3 GHz.

Example 1: Breaking cyclohexanol-water emulsion

Cyclohexanol has a density of 0.95 g/ml. Two similar emulsions were prepared:

A) Cyclohexanol (15 ml)  
Water (50 ml)

B) Cyclohexanol (15 ml)  
Water (50 ml)

The average radius of the vesicles (r) is: \( r \approx 1 \mu m \).

Surface tension (\( \gamma \)):  
0.04 N/m = (40 dyne/cm)

Density (\( \rho \)):  
0.95 g/ml

The average excitation frequency is calculated according to formula 1:

\[ v = \frac{1}{\pi} \times \sqrt{\frac{5 \times 0.04}{(6 \times 10^{-6})^3 \times 0.95 \times 10^{-3}}} = 1.9 \text{ GHz} \]

This means that a domestic microwave oven having a magnetron operating at 2.24 GHz is well-suited for water/"oil" emulsions of the above composition.

Each of the mixtures were placed in a separation funnel. Both mixtures were shaken vigorously for 15 sec after which a white emulsion (like milk) was produced. A) was placed in the hood for separation and B) were placed in the microwave oven. In the microwave oven were placed water containers (2 L) to absorb microwaves. B) was irradiated for 15 sec and then for 40 sec. The temperature increased to 42 °C. The whole procedure took 4
min. The mixture is poured gently back into the separation funnel and 13.5 ml of cyclohexanol could be obtained. The isolated cyclohexanol appeared clean and was cleared from water. A) was after the initial mixing placed in a water bath at 40 to 45 ºC. After 40 min a clear phase boundary between the two phases was not distinguishable but 11.5 ml of turbid cyclohexanol could be isolated. After 65 min 12.4 ml turbid cyclohexanol could be retained.

Example 2: Breaking cyclohexylchloride-water emulsion

Cyclohexylchloride (30 ml) was placed in a round-bottomed flask (250 ml) and concentrated hydrochloric acid (120 ml) was added. The mixture was heated to reflux for 2 h. After this the solution was cooled to room temperature and poured into a separation funnel. The aqueous phase was separated from the organic layer that was extracted with concentrated sulphuric acid (10 ml). The mixture was warmed by this manipulation and a red/orange mixture was produced. The phases were separated for 15 min. The sulphuric acid was removed and the organic phase was extracted with water (20 ml). At this point, a very dense emulsion was produced and based on the literature (page 163 in "Experimental Methods in Organic Chemistry", James A. Moore, David L. Dalrymple, and Oscar R. Rodig, CBS College Publishing, 3th edition, 1983), it was recommended to let it stand over night for separation. The reason for the dense emulsion was that several products, with very different polarity, are produced during work-up. Water was, however, added to a total volume of 70 ml and the emulsion was divided in two fractions of 35 ml.

The average radius of the vesicles (r) is: ≈ 1 μm.

Surface tension (γ): 0.04 N/m = (40 dyne/cm)

Density (ρ): 0.95 g/ml

The average excitation frequency is calculated according to formula I:

\[ v = \frac{1}{\pi} \times \sqrt{\frac{(5 \times 0.04)/(6 \times (10^{-6})^3 \times 0.95 \times 10^{-3})}{}} = 1.9 \text{ GHz} \]

This means that a domestic microwave oven having a magnetron operating at 2.24 GHz is well-suited for water/"oil" emulsions of this composition.

The same set-up and procedure as in Example 1 was used. After 45 sec of MW irradiation of B) are the phases well separated with a clear organic phase. Immediately after irradiation, 9.5 ml cyclohexylchloride was isolated by phase separation in the separation funnel. The total time for the separation was 4 min. A) was left for 3 h at 30-45 ºC after which the boundary seemed clear but the organic phase was clearly turbid. 8 ml of turbid cyclohexylchloride could be retained.
Example 3: Breaking mineral oil-water emulsion

The same type of experiment as in experiments 1 and 2 was set-up. Mineral oil (10 ml) was mixed with water (25 ml). B) was irradiated for 45 sec and 8 ml of mineral oil could be retained. After 1 h, A) was only scarcely separated.

The average radius of the vesicles (r) is: 0.5 µm
Surface tension (γ): 0.042 N/m = 42.0 dyne/cm
Density (ρ): approx. 0.8 g/ml

In formula:

\[ v = \frac{1}{\pi} \times \sqrt{\frac{(5 \times 0.042) / (6 \times (0.5 \times 10^{-6})^3 \times 0.8 \times 10^{-3})}{}} = 0.19 \text{ GHz} \]

Thus, a domestic microwave oven, although far from optimal, could be used due to the fact that the size (radius) distribution was fairly broad.

Example 4: Breaking cyclohexanone-water emulsion

Cyclohexanone (10 ml) and water (35 ml). The set-up was the same as in Examples 1 and 2. B) was irradiated for 60 sec and 8.5 ml cyclohexanone was recovered. This manipulation takes 4 min. At this time A) appears as a dense emulsion. A) was placed in a water bath 40–50 °C for 30 min. After 47 min 6.5 ml cyclohexanone could be recovered from A).

Example 5: Breaking mineral oil-ethanol emulsion

Mineral oil (10 ml) and ethanol (25 ml) was used in a similar set-up as in Examples 1 and 2. B) was irradiated for 30 sec and 9.5 ml of mineral oil could be recovered after 4 min. A) was placed at 40–50 °C for 10 min after which no clear boundary between the two phases could be observed.

Example 6: Breaking olive oil-water emulsion

Olive oil (10 ml) and water (25 ml) was used in a similar set-up as in Examples 1 and 2. B) was irradiated for 1 min and after a total of 5 min could 9.5 ml of olive oil be recovered. At this time no clear boundary between the phases in A) could be observed. After 35 min 9 ml olive oil from A) could be recovered.

Example 7: Manipulation of alumina nano-particles

Alumina (Al₂O₃-γ) was used in this experiment. These nano-particles were produced by flame burning, collected on a filter and weighted before it was brought in a domestic microwave oven of 2.24 GHz and 700 W for 2, 5, 10 and 15 minutes. These irradiated samples were diluted in ethanol and dried on a copper grid for later analysis by TEM.
It is important when investigating a new material that we make use of the formula derived above, in the Theory section, in which the frequency of the applied radiation is related to the particle size. If, on the other hand, we increase the particle size, we can verify the formula.

The investigation has shown a difference in the form of clustering of the aerosols between those irradiated and not irradiated particles, as it is shown in Figures 2a and 2b. According to the theory, explained in the Theory section, we expect the surface tension to be larger in the case of emulsion, where the effective frequency of radiation is expected to be above 2 GHz.

Diffraction patterns of the irradiated particles reveal an amorphous phase together with a crystalline phase, while it appears in a completely amorphous phase when it is not irradiated. This comparison can be seen in Figure 1.

Suspensions

Example 8: Colloidal Iron(III)

Multinucleated complexes are formed when Fe(III) is dissolved in water. This leads to formation of a macro ion which can be described as: \( (n\text{Fe(OH)}_2\text{aq.mH}^+) \), i.e. colloidal iron with adsorbed protons. A diluted Fe(III)Cl will upon heating turn red/orange due to the formation of the ferrihydroxy sol.

Water (25 ml) was placed in a conical flask and radiated for 1.5 min with microwaves (2.4 GHz, 600 W). The temperature was increased to about 75 deg. Fe(III)chloride (50 mg) was placed in the flask and the solution was set aside. To another flask Fe(III)chloride (50 mg) was dissolved in water (25 ml), placed in the microwave oven, and the solution was radiated for 1.5 min. The solution turned red/orange within a few seconds after radiation was initiated. The non-radiated Fe(III)chloride remained yellowish. The next day, a precipitate has formed in both flasks and a sample was taken out from both flasks and analysed with electronmicroscopy (EM). The EM pictures showed that the precipitated material from the microwave-radiated suspension precipitated as small loosely interconnected "crystals" whereas the non-irradiated suspensions precipitated as a precipitate "cake" i.e. as larger integrated structures. Clearly the microwaves have an effect on the structure of precipitated material in favor of a more uniform precipitate.

The average excitation frequency can be calculated according to formula II

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (r)</td>
<td>0.01-0.001 µm</td>
</tr>
<tr>
<td>Young module (E)</td>
<td>Approx. 50 g/cm²</td>
</tr>
<tr>
<td>Density (ρ)</td>
<td>6.5 g/cm³</td>
</tr>
</tbody>
</table>
\[ N = 1/(a \times \pi) \times \sqrt{E/\rho} = 0.1 - 1 \text{ GHz} \]

Again, a magnetron with radiation of 2.24 GHz can be used for aqueous dispersed particle of
the above characteristics, although not fully optimal.

**Example 9: Precipitation of heavy metals from sewage solutions**

An important application of microwave radiation is the treatment of sewage where the
microwaves can help extracting heavier elements that cause environmental problems in
the treatment of sewage in sewerage stations. Sewage solutions of deferent concentrations
have been studied by scanning electron microscopy, SEM, to see if microwave treatment of
the solutions could enhance the precipitation of heavier metals and change the structure of
the sewage materials. The electron microscope had attached an EDAX X-ray aggregate to
facilitate chemical studies of the sewage parallel to scanning pictures of the structure. The
sewage samples were extracted and delivered from a sewerage station in Copenhagen.

The sewage was diluted from 1 to 250 times in chlorinated water, one being diluted 2
times, the next 10 times diluted, the third 50 times diluted and the last 250 times diluted.
The samples for SEM studies were extracted from the middle of the containers and
sputtered (evaporated) with a thin platinum layer. A series of samples were extracted
before the containers were treated with microwaves and another series extracted after
microwave treatment so that the microwave irradiation would not interfere with the
platinum layer. The microwave radiation was delivered by a standard magnetron at
2.24 GHz and resulted in a temperature increase of less than 5 °C.

The samples that were most altered by microwave radiation were the ones with the lowest
dilution. The studies clearly showed, see Figures 3a-3d, that microwaves with a small
thermal component altered the structure of the sewage causing a higher degree of
aggregation. The chemical analysis from the EDAX measurements clearly showed that
microwave irradiation caused a strong precipitation of heavier metals and other heavy
chemical elements (see Figure 3c). Particularly the EDAX spectrum showed pronounced
peaks of Iron, Phosphate and Cu in the material that was microwave treated while none of
these elements were seen in the untreated samples. The heavier metals were identified on
the surface of spherical aggregated clusters thus making it easy to extract these metallic
elements. The important results from these studies thus confirm that microwave irradiation
can help extracting heavier elements from sewage that otherwise cause environmental
problems.
Example 10: MW irradiation of Diesel emission

The effect of the primary modulation was tested on Diesel exhaust gas. The exhaust gas was lead through a plastic pipe to a microwave oven. Samples were taken immediately before the inlet to the oven (1) and samples were taken immediately after the outlet of the oven (2). The exhaust gas is MW treated in the order of seconds. The samples were analysed by scanning electron microscopy.

Samples from 1 (Figure 4a) show a rather dispersed distribution of particles among which the majority of the particles are very small (10-50 nm), and much fewer larger aggregates are seen. Samples from 2 (Figure 4b) show a different distribution pattern of the particles. Nearly no small particles can be detected and only aggregates of much larger size is observed. The experiments illustrate that the aggregation of the small particles can be accelerated significantly by MW treatment.
CLAIMS

1. A method for manipulating a dispersed system, said dispersed system comprising a dispersing medium and a dispersed phase, said dispersing medium and dispersed phase independently being a solid, a liquid or a gas, where said dispersed phase is constituted by a plurality of phase members, the method comprises the step of treating the dispersed system with a primary manipulator in the form of electromagnetic radiation in order the change the properties of the phase members, and subsequently treating the dispersed system with a secondary manipulator in order to facilitate sedimentation/fusion of the phase members.

2. The method according to claim 1, wherein the electromagnetic radiation (the primary manipulator) is applied as defined in any one of the claims 27-32.

3. The method according to any one of the preceding claims, wherein said electromagnetic radiation (the primary manipulator) has a frequency in the range of 0.001-1000 GHz.

4. The method according to any one of the preceding claims, wherein said secondary manipulator is an electric field of in the range of $1.0 \times 10^5$ V.

5. The method according to any one of the claims 1-4, wherein said secondary manipulator is a magnetic field of in the range of $10^{-6}$-$10^{-2}$ Tesla.

6. The method according to any one of the claims 1-4, wherein said secondary manipulator is an electromagnetic wave (light) of a wavelength in the range of 10-10,000 nm.

7. The method according to claim 6, wherein said electromagnetic wave is a LASER.

8. The method according to any one of the claims 1-7, wherein the dispersed system is an aerosol/smoke where the dispersing medium is a gas and the dispersed phase is a solid (particles).

9. The method according to claim 8, wherein the particles of the aerosols/smoke are subsequently subjected to a filtration step in order to remove at least a portion of said particles from said gas.

10. The method according to claim 9, wherein the filtration is performed by a mechanical filter.
11. The method according to claim 9, wherein the filtration is performed by an electromagnetic wave.

12. A method for manipulating a dispersed system, said dispersed system comprising a dispersing medium and a dispersed phase, said dispersing medium being a gas and said dispersed phase being a solid, where said dispersed phase is constituted by a plurality of phase members (particles), the method comprises the step of treating the dispersed system (an aerosol) with a primary manipulator in the form of electromagnetic radiation in order to change the properties of the particles in order to facilitate sedimentation/fusion of said particles so that the particles can subsequently be removed from the dispersing medium (the gas).

13. The method according to claim 12, wherein the electromagnetic radiation is applied as defined in any one of the claims 27-32.

14. The method according to any one of the claims 12-13, wherein said electromagnetic radiation (the primary manipulator) has a frequency in the range of 0.001-1000 GHz.

15. The method according to any one of the claims 12-14, wherein the particles of the aerosol are subsequently subjected to a filtration step in order to separate at least a portion of said particles from said gas.

16. The method according to claim 15, wherein the filtration is performed by a mechanical filter.

17. The method according to claim 15, wherein the filtration is performed by an electromagnetic wave.

18. A device for removal of particles from aerosols/smoke in a continuous manner, said device comprising a conduit for passage of the particles of said aerosol/smoke, and means for application of electromagnetic radiation to said particle upon passage of said conduit.

19. The device according to claim 18, which further comprises means for application of an electric field of in the range of 1.0-10^6 V to said conduit.

20. The device according to claim 18, which further comprises means for application of a magnetic field of in the range of 10^6-10^2 Tesla to said conduit.
21. The device according to claim 18, which further comprises means for application of an electromagnetic wave of a wavelength in the range of 10-10,000 nm to said conduit.

22. The device according to claim 21, wherein said electromagnetic wave is a LASER.

23. The device according to any one of the claims 18-22, which further comprises means for mechanical filtration.

24. The device according to any one of the claims 18-23, which comprises means for application of an electric field of in the range of $1.0 \times 10^6$ V and/or means for application of a magnetic field of in the range of $10^{-6}-10^{-2}$ Tesla in combination with means for application of an electromagnetic wave (light) of a wavelength in the range of 10-10,000 nm.

25. An exhaust system of a combustion engine which comprises a device as defined in any one of claims 18-24.

26. The exhaust system according to claim 25, wherein said combustion engine is a Diesel engine.

27. A method for manipulating a dispersed system, said dispersed system comprising a dispersing medium and a dispersed phase, said dispersing medium and dispersed phase independently being a solid, a liquid or a gas, where said dispersed phase is constituted by a plurality of phase members, and where

when the dispersing medium is a liquid and the dispersed phase is a liquid (emulsion), the phase members are in the form of vesicles (surrounded by the dispersing medium), such vesicles initially (before application of electromagnetic radiation) being characterised by the radius ($r$) of the vesicles, the surface tension ($\gamma$) of the vesicles and the density ($\rho$) of the material constituting the vesicles,

when the dispersing medium is a liquid and the dispersed phase is a solid (suspension), the phase members are in the form of particles (surrounded by the dispersing medium), such particles initially (before application of electromagnetic radiation) being characterised by the radius ($r$) of the particles, the Young's modulus ($E$) of the particles and the density ($\rho$) of the material constituting the particles, and

when the dispersing medium is a liquid and the dispersed phase is a gas (foam), the phase members are in the form of gas bubbles (surrounded by the dispersing
medium), such bubbles initially (before application of microwave radiation) being
characterised by the radius \( r \) of the bubbles, the surface tension \( \gamma \) of the
bubbles, the density \( \rho \) of the material constituting the bubbles, and the difference
\( \Delta \rho \) between the inner and the outer pressure of the bubbles;

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the method comprising applying electromagnetic radiation having a frequency in the range
of \( 1/12 \) to \( 12 \) times the estimated average excitation frequency, \( \nu \), where

when the dispersing medium and the dispersed phase are both liquids, the average
excitation frequency, \( \nu \), for the vesicles of the dispersed system before application
of electromagnetic radiation is estimated by the following formula I

\[
\nu = \frac{1}{\pi} \times \sqrt{\left( \frac{5 \times \gamma}{6 \times \rho \times r^3} \right)}
\]

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when the dispersing medium is a liquid or air and the dispersed phase is a solid
(suspension, aerosols), the average excitation frequency, \( \nu \), for the particles of the
dispersed system before application of electromagnetic radiation is estimated by
the following formula II

\[
\nu = \frac{1}{(r \times \pi)} \times \sqrt{\left( B \times \frac{r}{\rho} \right)}
\]

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and when the dispersing medium is a liquid and the dispersed phase is a gas
(foam), the average excitation frequency, \( \nu \), for the particles of the dispersed
system before application of electromagnetic radiation is estimated by the following
formula III

\[
\nu = \frac{1}{\pi} \times \sqrt{\left( \frac{5 \times (\gamma - \Delta \rho \times r)}{6 \times \rho \times r^3} \right)}
\]

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28. The method according to claim 27, wherein the duration of the application of electro-
magnetic radiation is so that the obtained average vesicle/particle/bubble radius is
between \( 1.1 \) to \( 10 \) times of the initial average vesicle/particle/bubble radius.

29. The method according to any one of the claims 27-28, wherein the application of
electromagnetic radiation is conducted under conditions where any increase in temperature
is at the most \( 20 \) K.
30. The method according to any one of the claims 27-29, wherein the frequency of the electromagnetic radiation is in the range of 1/8 to 8 times the estimated average excitation frequency.

31. The method according to any one of the claims 27-30, wherein the frequency of the electromagnetic radiation is gradually lowered corresponding to the increase in the vesicle/particle/bubble size, in particular in such a manner that the frequency of the electromagnetic radiation is at any time in the range of 1/12 to 12 times the existing estimated average excitation frequency.

32. The method according to any one of the claims 27-30, wherein more than one average frequency is determined for disperse systems containing particles/vesicles of different sizes.

33. A method for the separation of heavy metal constituents from sewage solutions, said method comprising

   a) obtaining a sewage solution,
   b) applying electromagnetic radiation to said solution, and
   c) isolating the heavy-metal enriched precipitate from said electromagnetic radiation treated sewage solution.
Fig. 1
Fig. 2
Fig. 4a
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7  B01D17/04  C10G33/02

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)

IPC 7  B01D  C10G

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

Electronic database consulted during the international search (name of database and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Date of the actual completion of the international search: 30 August 2004

Date of mailing of the international search report: 06/09/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk
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