

The invention relates to a method for the production of microcapsules through the microencapsulation of hydrophobic oils with substances dissolved or dispersed therein, especially colour reaction partners of colour reaction systems, whereby a hydrophobic oil containing the substance in dissolved or dispersed form is mixed, under vigorous stirring with an aqueous medium, to yield aminoplast capsules in the resultant oil-in-water dispersion under acid conditions, with the said aminoplast capsules subsequently isolated where desired, whereby at least one dispersion-stabilising compound which is not a reactive tenside is contained in the acid-adjusted oil-in-water dispersion.

A method of the above type is known from DE-A-38 18 712. The method is based on the fact that the aqueous medium contains, for the purpose of stabilising the dispersion, a water-soluble, anionic sulphonated melamine-formaldehyde precondensate and such a water-soluble cationic compound as to together interact to form a dispersion-stabilising compound. A cationic melamine-formaldehyde precondensate is preferred as the interacting cationic compound, especially one which is an oligomer with 2 to 6 triazine rings, with 2.5 to 5 methylol groups per triazine ring and free of methylol ether groups. This method permits the derivation of high quality dry individual capsules as a result of the exclusion of film-forming polymers. These individual capsules can be redispersed in advantageous solvents. The resultant dispersions are optimally suited to printing, especially segmental printing methods such as flexography, screen printing and rotogravure so that capsules are only applied at those points where copying procedures actually take place. This method is dependent on the fact that the dispersion-stabilising compound or dispersion-stabilising complex is produced within the framework of interaction between two different reaction partners. In particular cases the production of the dispersion-stabilising compounds requires a high-performance dispersion apparatus to achieve especially pronounced turbulence. The aforementioned cationic compounds as interacting reaction partners of the dispersion stabilization are as a rule expensive and have only a limited shelf life. Consequently, they have to be used shortly after delivery, thereby adversely affecting the flexibility of the process.

The aim of the invention was thus to improve the above method such that the stabilization of the dispersion is a relatively simple process which dispenses with the need for a water-soluble cationic compound.

The aim according to the invention is achieved by virtue of the fact that the oil-in-water dispersion contains A) a water-soluble, anionic, sulphonated melamine-formaldehyde precondensate and/or B) a water-soluble, anionic, modified melamine-formaldehyde precondensate, and has been derived by

a) reacting, in a first step, melamine and formaldehyde at a temperature between 75 and 100°C in an alkaline medium in the presence of water with at least one compound (I) in the form of an alkali sulphite, an alkaline earth sulphite, an alkali sulphamate, an alkaline earth sulphamate, an aminosulphonic acid, an aminocarboxylic acid or an aminodicarboxylic acid, to form a precondensate

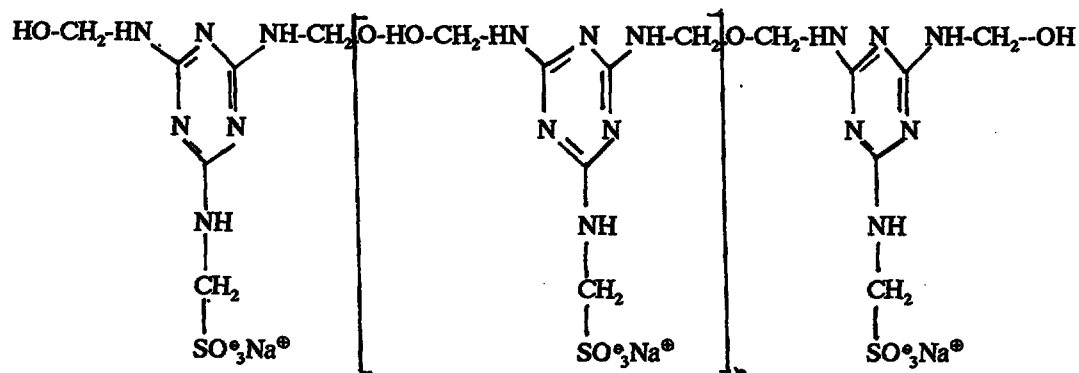
b) subsequently, in a second step, subjecting this precondensate to a polycondensation reaction at a pH of approximately 5.5 to 7.0 by rendering it acidic through the addition of at least one acidic compound (II) in the form of a sulphamic acid, an aminocarboxylic acid, an aminodicarboxylic acid, a hydroxycarboxylic acid, a polyhydroxycarboxylic acid or an aminosulphonic acid, and

c) once the polycondensation reaction is complete, rendering the resultant resin solution alkaline through the addition, if necessary, of at least one basic compound (III), and
d) incorporating this, if necessary alkaline, resin solution for stabilization of the dispersion into the process, whereby the compounds A) and B) alone act to stabilise the dispersion and no water-soluble cationic compound is used for this purpose.

Thus, the principle of the method according to the invention is that stabilization of the aqueous dispersion, in which the capsule wall formation mechanisms occur, is mediated by at least one of the two compounds A) and B). No further reaction partners are necessary to stabilise the dispersion.

In the preferred embodiment of the invention, the hydrophobic oil, containing a given active ingredient, especially in the form of a colour-forming agent of a colour reaction system, is stirred into an acidified aqueous medium containing one of the two compounds A) or B), or mixture thereof, used for stabilising the dispersion. This is preferably carried out with vigorous stirring. It has been demonstrated that the dispersion-stabilizing compounds develop their full efficacy in this acid medium. The shearing forces have to be sufficient upon stirring to achieve the desired fine dispersion of the hydrophobic oil droplets in the aqueous phase. To date it has been assumed from the state of the art, represented, inter alia, by DE-A-38 18 712, that the water-soluble, anionic, sulphonated melamine-formaldehyde precondensate is not on its own suited to stabilise the dispersion. This holds for the production of the oil-in-water dispersion described above since the commercially available products (liquid dispersions) are alkaline in nature. If the hydrophobic oil is stirred vigorously into such alkaline media then the emulsion will break down immediately upon cessation of stirring. A two-layer structure forms within a very short period of time. Surprisingly, it has been shown that if the vigorously stirred aqueous medium is acidified, for instance by reducing the pH to below 6.5, then an emulsion is derived which is stable over long periods. It was further surprising that following addition of the wall-forming materials to derive the aminoplast shells, this, with respect to wall formation, reactive oil-in water emulsion did not break down or undergo any other negative change, even if capsule wall formation had reached a stage in which solid particles had been formed. In other words, the desired stabilisation during the entire process is achieved through stabilization in an acid medium according to the method solely through the use of the aforementioned compounds. There is one exception in the state of the art wherein an original melamine-formaldehyde precondensate is precipitated out in an extremely fine suspension and the emulsification effected in this very fine suspension (cf. DE-A-37 09 586).

The water-soluble, anionic, sulphonated melamine-formaldehyde precondensates used within the framework of the invention have been described in, for example, DE-A-38 18 712 and in the journal "Zement-Kalk-Gips", Bauverlag, Wiesbaden, Volume 21 (1968), No. 10, pages 415-419. The melamine-formaldehyde precondensate used according to the invention preferably contains an average of approximately 0.7 to 1.3, and especially 0.9 to 1.1, sulphonate groups per melamine ring. The melamine ring preferably contains approximately 2 to 4, and especially approximately 2.5 to 3.5 methylol groups. The molecular weight of the sulphonated melamine-formaldehyde precondensate is preferably in the range 3,000 to 300,000 and especially approximately 5,000 to 100,000. Its ideal structure is



wherein n is preferably a whole number between 8 and 1000 and especially between approximately 15 and 350. No special importance is attached to the sodium ion in this formula and it can be replaced through any other metal ion which ensures the water-solubility of this precondensate.

Modified melamine-formaldehyde precondensates such as those described in EP-B-0 059 353 and above as compound B) may be used in place of the water-soluble, anionic, sulphonated melamine-formaldehyde precondensates described in detail above for stabilization purposes in the acidic medium. As far as the procedures subsequent to the production of B) are concerned, the use of this system described by the parameters of the method does not differ from that of the water-soluble, anionic, sulphonated melamine-formaldehyde precondensate. The derivation of the second compound B) used according to the invention is preferably as follows:

In the first step (a) of the method for the production of the modified melamine-formaldehyde precondensate B) to be used according to the invention, formaldehyde is used as the aldehyde, either in the form of a gas, or solution, preferably in the form of aqueous solutions, or in solid form, for example as paraformaldehyde.

In the first step of the production of compound B), the melamine, the formaldehyde and the compound (I) are preferably used in a molar ratio of approximately 1:3.5 to 6:0.5 to 1. The pH for the first step is preferably between approximately 9.0 and 13.0, with the reaction temperature between 75 and 100°C. Melamine is in general poorly soluble, for instance in water, below 75°C. Above 100°C, the exothermic reaction of the first step generally proceeds so rapidly that undesirable quantities of insoluble resin may be produced.

In the second step (b), the precondensate from the first step and the compounds from group (II) are preferably used in a molar ratio of 1:0.1 to 3 with respect to the melamine used in the first step. It is especially advantageous to use a mixture of sulphamic acid and glutamic acid, in particular a mixture of equal parts by weight of sulphamic and glutamic acid, as the group (II) compound for the second condensation step. In the second step (b), addition of compound (II) changes the pH to approximately 5.5 to 7.0 and causes the polycondensation reaction to proceed further, whereby the acidic compound used is incorporated into the resin molecule so that the polymer molecule is thereby modified. The pH should not drop too far below roughly 5.5. With a value, for instance, of approximately 4.5 there is the danger that the reaction between 75 and 100°C would proceed so rapidly that undesirable quantities of insoluble solid resin would result. The basic compound (III) is preferably an alkali hydroxide, an alkaline

earth oxide, an alkaline earth hydroxide, an amine, a polyamine, a monoethanolamine, a diethanolamine, a triethanolamine and/or a basic metal compound.

The method of deriving the modified melamine-formaldehyde precondensate used according to the invention is preferably controlled with respect to the starting materials and process parameters such that the substituent groups in the melamine basic structure have the groups $\text{-NH(CH}_2\text{)}_6\text{COOH}$ and/or $\text{-NHSO}_3\text{H}$. The preferred examples of aminocarboxylic acids are aminoacetic acid (glycine) and aminopropionic acid (alanine), the preferred hydroxycarboxylic acids are glycolic acid and lactic acid., the preferred polyhydroxycarboxylic acid is gluconic acid and the preferred aminodicarboxylic acids are aspartic acid and glutamic acid.

The solutions of melamine-formaldehyde resins B) derived by the described methods and used for stabilization of the dispersion according to the invention may be either diluted and concentrated; in particular they may be spray dried and at a later point in time dissolved again. The method is generally carried out at ambient pressure. It may, however, be carried out under excess pressure or negative pressure (vacuum).

Irrespective of whether a compound of type A) and/or B) described above is used for the various embodiments of the invention, it is surprising that an improvement in the quality of the capsules is achieved. This is manifested in a reduced leakage through the capsule walls/reduced migration, so that undesired premature coloration is to a very large extent ruled out if the capsules are used for reaction copying papers.

Regardless of whether compound A) and/or compound B) is used, the desired effects are favoured by the presence in the reaction medium of metallic compounds, for instance the phosphate, chloride, nitrate, sulphate, acetate and the like of bivalent metals such as calcium, magnesium, zinc or metals with other valencies such as aluminium, iron, nickel, cobalt and/or manganese, silicon, zircon and titanium. The metals may also be introduced into the aqueous medium in the form of their carbonates, oxides or hydroxides if no other anions are to be present. In special cases it can be advantageous to introduce metals in the form of complexes. As a rough guide, the aforementioned salts or compounds to achieve the desired effects should be present at a concentration of approximately 0.1 to 12 per cent by weight with respect to the aqueous component of the particular dispersion. The range from approximately 0.5 to 6 per cent by weight is especially preferred.

The intention of the invention is still retained if further substances which in some way bring about an improvement in the method are also added. It may thus be advantageous to introduce polymers in particular cases to achieve certain effects, such as to prevent sedimentation or control the viscosity or rheology of capsule dispersions. The polymers may especially be ones bearing acid, amide, amino, imino, ester, ether, hydroxyl, urethane, thiol (mercaptan) groups, especially polyvinylalcohol, gelatine and copolymers of maleic anhydride. Various other additives may also be added to the reaction medium, such as an ammonium salt, eg., ammonium chloride, which in some cases may accelerate the condensation reaction.

Of decisive importance for the method according to the invention is that the dispersion-stabilizing compounds, as described above, are present in the reaction system at least whilst the actual capsule-forming process is proceeding. It has been shown to be of especial advantage if the original basic aqueous starting media of compounds A) and/or B) are

acidified and the inert hydrophobic oil containing the actual active ingredients, especially in the form of the colour-forming agents of colour reaction systems in dispersed form, are worked into this acid phase under vigorous stirring. The shearing forces applied during stirring must be adequate to ensure the production of a fine emulsion which is necessary for the subsequent steps. On the other hand, the relevant hydrophobic phase containing the desired active ingredient may be mixed into the original alkaline aqueous medium containing the compounds A) and/or B) under the required stirring conditions, and the pH subsequently adjusted to a value below 7 through the addition of acidifying compounds under further stirring. The resultant emulsion has the necessary stability below pH 7 and does not lose it when the substances necessary for subsequent process steps, especially the compounds necessary for wall formation, are added under conditions with which the expert is familiar. The basic concept of the present invention is thus satisfied when the reactive emulsion is formed and contains all the substances necessary for wall-forming mechanisms and the compounds needed for stabilization. Vigorous stirring is no longer possible once the wall-forming materials have been added since this would have a negative effect on the formation of the capsule wall envelope. Consequently, all the measures required for stabilization, especially the addition of compounds A) and/or B) must normally be complete by the time the wall-forming mechanisms commence.

The nucleus of the invention is not the manner in which the aminoplast capsules are formed. The usual methods may be adopted for this. The aminoplasts may thus, for instance, comprise aldehyde condensates based on melamine, urea, thiourea, N-alkylurea, guanidine, acetoguanamine, benzoguanamine, caprinoguanamine, cyanamide, dicyandiamide or alkyl/arylsulphonamide. The preferred aldehyde is formaldehyde; higher aldehydes may also be used, however.

The expert will be aware that the properties of the aminoplast capsule shell can be influenced to a large degree both through the starting substance in the form of the water-soluble aldehyde precondensate or mixtures of chemically different precondensates, as well as through the process characteristics/control of the condensation reaction. Reference is made in the relevant literature to the control parameters for aminoplast condensation such as the pH, acid type, temperature and concentration of the reaction resins or further constituents of the reaction medium.

Non-ionogenic melamine-formaldehyde precondensates have been found to be especially suited to the formation of the aminoplast capsule shell. Various requirements must be fulfilled here. First it needs to be water-soluble. Secondly its intrinsic reactivity should be reduced. This reduction can be achieved through at least partial blocking of the active methylol groups. Suitable methods for this are known (see "Kunststoffhandbuch", Vol. X, Duroplaste, page 173). The desired reactivity of the non-ionogenic oligomeric melamine-formaldehyde precondensate can thus be adjusted through partial methylation. Such a product is described in EP 00 26 914. This contains, for example, 5.25 moles of formaldehyde and 2.3 moles of methylether groups per mole of melamine. These requirements are for the most part satisfied by the commercial products - Madurit MW 112® available from Cassella AG (compare here "Synthetic resins - Hoechst, Technical Data Sheet", September 1992), BC 336® from BIP Chemicals Ltd and Resin 42-91® from Rousselot GmbH.

The reduction in reactivity of the non-ionogenic melamine-formaldehyde precondensate

ensures that the encapsulation process does not proceed too rapidly. This in turn prevents undesired agglomerate formation or flocculation of larger particles. Agglomerates or large particles would lead, for instance, to illegible print in reaction copying papers. Non-ionogenic methylated melamine-formaldehyde precondensates with the aforementioned degree of methylation in general possess the desired reactivity and are therefore preferred in the context of the invention. Mixtures of non-ionogenic melamine-formaldehyde precondensates of varying reactivity can also be used for the purpose of the invention. In particular cases it can be advantageous to modulate the reactivity of the non-ionogenic melamine-formaldehyde precondensate which is available through the addition of formaldehyde.

The concentration for use of the aqueous solution of the non-ionogenic melamine-formaldehyde precondensate may vary between wide limits and is preferably between approximately 7 and 20 per cent by weight and lies in particular in the region of 12 per cent by weight.

The hydrophobic oil in which, for instance, the colour-forming agent of a colour reaction system or its acid reaction partner is dissolved - insofar as this is a soluble compound (such as a phenolic compound), is inert with respect to water, i.e., is practically insoluble in water/immiscible with it. Any minimal solubility can be neglected. Preferred examples of oils which can be used according to the invention as solvents for the colour reaction partners are especially partially hydrogenated terphenyls, chlorinated paraffins, alkylated biphenyls, alkyl naphthalene, halogenated olefins, derivatives of diaryl methane, derivatives of dibenzylbenzole, alkanes, cycloalkanes and esters such as phthalates, adipates, trimellitates and phosphates.

Numerous colour-forming agents, described in the specialist literature in detail, can be dissolved in the hydrophobic oils and for encapsulation. Examples of these are derivatives of lactone, phthalide, fluoran, diphenylamine, spiropyran, auramine, phenothiazine, aminophenylpyridine and aminodiazaxanthene lactone. Although the invention in particular takes account of a method for the microencapsulation of hydrophobic oils with the colour reaction partners of colour reaction systems dissolved therein, it is obvious that the principle of the invention equally applies if other agents are mixed into the hydrophobic oil or if other agents, such as fragrances and aromatic agents, flavourings, vitamins, fertilisers, insecticides, insect-attracting agents, fungicides, crop protection products, cleaning agents, solvents, lubricants, fluorescent agents, liquid crystals, adhesives, explosives and gas-forming compounds for single and multi-component systems, colour pigment dispersions and magnetic pigment dispersions in oil or wax carrier materials, are encapsulated on their own.

The following procedure is preferably adopted for the method according to the invention using the water-soluble, anionic, sulphonated melamine-formaldehyde precondensate A) or compound B) alone for stabilization of the dispersion: an aqueous alkaline solution (pH approximately 9 to 10), of the order of 1 to 25, preferably approximately 4 to 10 per cent by weight, of the water-soluble, anionic, sulphonated melamine-formaldehyde precondensate A) or compound B) is adjusted to a pH below approximately 6.5, especially between approximately 3.5 and 5.5, through the addition of a suitable acid or acid salt, especially formic acid, phosphoric acid, sulphuric acid, acetic acid and the like. A hydrophobic oil with active ingredient dissolved or dispersed therein is then stirred into this solution with vigorous stirring, in particular through the use of a high-performance dispersion apparatus, for example that described in DE-PS 35 45 803. The weight ratio between the hydrophobic oil and the pre-

defined acidified medium containing the water-soluble, anionic, sulphonated melamine-formaldehyde precondensate A) or compound B) is approximately 1:100 to 30:20, preferably approximately 0.5:1 to 3:1.

The desired diameter of the oil droplets in the oil-in-water dispersion lies between approximately 2 and 10 micrometres, preferably between 3 and 7 micrometres. This diameter favours the uniform behaviour of the systems achieved through the derived microcapsules, especially colour reaction systems such as colour-reacting papers. If capsules are manufactured for applications other than colour-reacting paper then the capsule diameter may be increased considerably up to a few hundred micrometres. The ratio between the oil phase and the solid matter component of the aqueous phase chosen in each case is not critical. With colour-reacting paper capsules this weight ratio lies between approximately 2:1 and 9:1 especially between approximately 4:1 and 5:1. With capsules for other applications, the weight ratios may deviate considerably from the above numbers as required.

The mixture or oil-in-water dispersion is adjusted to the necessary acid pH value required for the condensation reaction, catalysed by acids, and proceeding during the later formation of the capsule shell either before or after addition of the oil phase. To this end, inorganic or organic acids or their salts may be used provided that they are acidic enough and do not give rise to any disruptive side effects and especially do not have a deleterious effect on the colour-forming agents of colour reaction systems in the hydrophobic oil. The preferred acids are acetic, formic, citric, nitric or sulphuric acid. The optimal pH for the condensation reaction generally lies in the weakly acid region, especially between approximately 3 and 6. The preferred range is approximately 3.5 to 5. If the pH is too high then the reaction time will be prolonged, and pH values which are too low should be avoided as these can lead, for instance, to premature coloration of the colour-forming agent in the microcapsule.

The aqueous solution of the non-ionogenic melamine-formaldehyde precondensate which subsequently forms the capsule shell is stirred, for example, into the mixture prepared in the aforementioned manner. The usual known stirring devices which do not give rise to special stirring or turbulence effects are suitable for this. The aforementioned high-performance dispersion apparatus must not be used for this since they would disturb the formation of the capsule shell through the condensation reaction of the non-ionogenic melamine-formaldehyde precondensate, where necessary with involvement of a water-soluble macromolecular substance.

The starting materials discussed in detail above are present exclusively in the form of a reactive oil-in-water dispersion or emulsion in which the shell of the microcapsule is formed under normal stirring within approximately 1 to 5 hours and especially within approximately 2 to 3 hours. This dispersion is completely stable as a result of the stabilization through compound A) and/or B).

Since the aforementioned condensation reactions leading to formation of the microcapsule wall are accelerated in the presence of heat it may be desirable to control or regulate the temperature of the individual process steps, for instance through warming. Once the reaction medium has formed, its temperature is generally adjusted to approximately 55°C to optimize the condensation reaction and thus microcapsule wall formation. This process is often virtually complete after allowing the reaction to proceed for two hours at approximately 55°C within

the preferred pH range described above. At a temperature below 55°C, microcapsules which are satisfactory in qualitative terms are also obtained in individual cases, although the reaction will require more time for completion, as mentioned above. Temperatures may therefore also be adopted which lie below or above approximately 55°C. The reaction temperature which is especially favourable for each particular case may be easily ascertained through simple experiment.

It may, in individual cases, be advantageous to control the method according to the invention by reducing the viscosity of the aqueous reaction system by the addition of a further water-soluble, anionic, sulphonated melamine-formaldehyde precondensate and/or compound B).

Once the condensation reaction is complete to the desired extent, the pH is neutralised or rendered weakly alkaline through the addition of alkali, especially sodium hydroxide, potassium hydroxide or ammonium hydroxide. This largely prevents any further reaction which could lead to agglomeration upon storage of the microcapsules. It further prevents corrosion of the metallic reaction vessels through the acid medium. If ammonium hydroxide is used then any free formaldehyde present will be largely removed from the reaction system as an odourless addition compound.

The method according to the invention may be carried out in batches or as a continuous process. If continuous, then the aqueous solution obtained at the start of the process and containing the stabilising compound is preferably mixed after its production with the oil phase containing the active ingredient using a high-performance dispersion apparatus and then transferred to a mixing vessel cascade in which the condensation reaction proceeds, whereby the aqueous solution of non-ionogenic melamine-formaldehyde precondensate can be added in measured quantities to the first mixing vessel. It proves expedient in practice to introduce the reaction mixture firstly into one larger mixing vessel. Once this vessel is full, the fresh reaction medium is introduced into a second mixing vessel whilst the reaction in the first mixing vessel is proceeding to completion. The capsule dispersion is then removed when ready. Fresh reaction medium may then be introduced into the first reaction vessel whilst the capsule formation reaction is proceeding in the second mixing vessel. This continuous process is by way of example only and may be subject to numerous modifications.

Once the final aqueous capsule dispersion is complete it is subjected to the usual procedures to remove the aqueous component. This may be achieved, for instance, through filtration or centrifugation of the aqueous dispersion or through evaporation or spray drying of the aqueous component. Spray drying is especially suitable here. It is described for instance in Römpps Chemie-Lexikon, 7th edition, Vol. 6, 1977, pages 3693-4. The desired individual capsules result in all cases. There is also the option of initially transferring the aqueous dispersion into another water-free medium and to remove the aqueous component therefrom, so that the individual capsules are dispersed in the new medium. An example of such a method is the Flushing method, described for instance in Römpps Chemie-Lexikon, 8th edition, Vol. 2, 1981, pages 1346-7.

The advantages of the invention are as follows: the emulsion either containing or not yet containing the wall-forming materials can be stabilized solely through the stabilizing compound A) or B). No further compound, in the form of a water-soluble cationic compound, and especially in the form of a water-soluble melamine-formaldehyde precondensate which

can be rendered cationic, is required. This is only likely to be present in negligible quantities. This avoids an undesirable high formaldehyde load on the entire system. Finally, the use of an interacting polymer (with film-forming properties) is not necessary. The exclusion, at least to a large extent, of such a polymer enables individual capsules to be produced, ie., without agglomerate formation to any appreciable extent. Such individual capsules can be dissolved or dispersed in suitable solvents or liquid systems and are then especially suited to the production of high quality colour-reaction recording papers. These lend themselves to segmental printing. If the individual capsules are contained in predominantly anhydrous printing inks then they are especially suited to flexography, screen printing, wet and dry offset printing and rotogravure.

The invention is described in greater detail through the examples below:

Example 1

Ten parts by weight of a 40% aqueous solution of a sulphonated melamine-formaldehyde precondensate are diluted with 60 parts by weight of water at approximately 22°C. One ml of 20% formic acid is added to this under stirring with a normal paddle stirrer. The pH drops to 3.7 to 4.0. To this solution at approximately 22°C is added under stirring with a high-performance dispersion apparatus 54 g of an oily phase at 45°C which is obtained by dissolving 1.1 per cent by weight of 1,3-dimethyl-6-diethylaminofluoran, 0.4 per cent by weight of crystal violet acetone, 0.2 per cent by weight of 3,3-bis(1'-n-octyl-2'-methyl-indole-3'-yl)-phthalide, 2.4 per cent by weight of 2-octylamino-6-diethylaminofluoran, 0.3 per cent by weight of 9-N-butyl-carbazoyl-(3)-4,4"-bis(N-methyl-,N-phenylamino)-diphenylmethane and 0.6 per cent by weight of 10-benzoyl-3,7-bis-(dimethyl-amino)-phenothiazine in diisopropylnaphthalene. To the resultant stabile emulsion is added a solution of 3 g water and 1 g of 85% formic acid under stirring with a normal paddle stirrer, to yield a pH of approximately 3.1. To the stabile emulsion acidified in this manner is added a wall-forming solution comprising 12 g resin 42-91 (60% solution of a methylated melamine-formaldehyde precondensate in water) and 5 g water under continuous stirring, and the resultant mixture warmed to 55°C again with stirring, and then stirred for 4 hours at this temperature. After allowing it to cool to room temperature and adjusting the pH to pH 8.8 with 25% ammonium hydroxide a capsule dispersion results with capsules of approximately 3-8 micrometres diameter and a dry weight of approximately 38 per cent by weight.

Example 2

Six grams of calcium chloride were added under gentle stirring with a paddle stirrer to a solution obtained by mixing 211.5 g of water and 88.8 g of a 20% solution of a sulphonated melamine-formaldehyde precondensate. The pH was adjusted to approximately 3.8 with 4 ml of 20% formic acid. To this solution was added 417.3 g of oil phase at approximately 42°C under stirring with a high-performance dispersion apparatus, the said oil phase comprising 156.5 g chlorinated paraffin and 252 g kerosene as well as a total of 8.8 g colour-forming agent. The colour-forming agent was a mixture of 75% crystal violet acetone and 25% 9-N-butyl-carbazoyl-(3)-4,4"-bis-(N-methyl-,N-phenylamino)-diphenylmethane. The emulsion which resulted had a droplet diameter of approximately 3 to 10 micrometres which did not change significantly during the subsequent process steps.

The system was rendered acidic to a pH of approximately 3.1 by the addition of 10 g of a 20% aqueous solution of formic acid under gentle stirring. To this was added 131 g of a melamine-formaldehyde precondensate resin solution, formed from 50 g Urecoll SMV and 51 g water. The pH rose to 3.8.

After warming of the emulsion to 58°C and maintenance at this temperature for 3.5 hours with gentle stirring, a capsule dispersion formed which, following cooling and neutralization with 25% ammonium hydroxide to a pH of 8, contained capsules with a diameter of approximately 3 to 10 micrometres and the same properties as in Example 1 (no adhesion to substrates of various types, no restriction in the choice of binding agents, individual capsules formed upon spray drying or allowing the dispersion to dry, stable capsules, well suited to the production of coating mass for colour-reacting paper). The dry matter content of the dispersion was approximately 47 per cent by weight.

Example 3

84 g of a 20% solution of a modified melamine-formaldehyde precondensate, containing carboxyl groups, was diluted with 250 g water. 8 g of alum was added to this under stirring and the pH shifted to approximately 3.7. With the aid of a high-performance dispersion apparatus, 197 g of an oil phase was emulsified into it at room temperature, as described in Example 2. The emulsion had a droplet diameter of approximately 3 to 12 micrometres and remained stable during subsequent process steps.

The addition of 10 g of 20% formic acid to the emulsion under stirring with a paddle stirrer, followed by the further addition of a solution of 50 g of water and 55 g of a 70% solution of a methylolated melamine-formaldehyde precondensate and subsequent heating to 55°C, with maintenance of this temperature for 4 hours, yielded a capsule dispersion. This was allowed to cool and the pH adjusted to 7.5 through the addition of 25% ammonia solution. 7 g of ethylene urea was then added. After stirring for 1 hour, the pH had fallen to below 7. The pH was again adjusted to 7 through the addition of ammonium hydroxide.

The capsule dispersion could be spray dried to form a very loose, extremely finely powdered material.

Example 4

Derivation of the modified melamine-formaldehyde precondensate:

44.6 parts by weight (0.48 moles) of sulphamic acid and 56 parts by weight (0.44 moles) of melamine were sequentially added to a solution which comprised 130 parts by weight (1.6 moles) of 37% formalin, 120 parts by weight of water and 43.4 parts by weight of 50% sodium hydroxide solution. The mixture was heated to 80°C and then stirred for 60 minutes at this temperature. 2.6 parts by weight of 50% sodium hydroxide and then 19 parts by weight (0.1 mole) of sulphanilic acid were added to the resultant precondensate, whereupon the pH fell to 5.9. The reaction mixture was maintained at 80°C for one hour. It was then adjusted to pH 10.1 with sodium hydroxide and allowed to cool to room temperature. This yielded a

clear, colourless polymer solution with a dry matter content of 41% and a viscosity of 37 mPa.s.

Production of microcapsules:

50 g of the 41% aqueous solution of modified anionic melamine-formaldehyde precondensate derived according to the example above was diluted with 300 g of water at approximately 22°C and adjusted to a pH of approximately 4 with 20% sulphamic acid. To this was added, under stirring with a high-performance dispersion apparatus, 272 g of an oily phase at 45°C which was obtained by dissolving 1.1 per cent by weight of 1,3-dimethyl-6-diethylaminofluoran, 0.4 per cent by weight of crystal violet acetone, 0.2 per cent by weight of 3,3-bis(1'-n-octyl-2'-methyl-indole-3'-yl)-phthalide, 2.4 per cent by weight of 2-octylamino-6-diethylaminofluoran, 0.3 per cent by weight of 9-N-butyl-carbazolyl-(3)-4,4"-bis(N-methyl-,N-phenylamino)-diphenylmethane and 0.6 per cent by weight of 10-benzoyl-3,7-bis-(dimethyl-amino)-phenothiazine in diisopropylnaphthalene. A solution of 10 g of water and 0.3 g of 85% formic acid was added to the resultant stabile emulsion under stirring with a normal paddle stirrer, to yield a pH of approximately 3.2. A wall-forming solution comprising 70 g of a 60% solution of a methylated melamine-formaldehyde precondensate in water (marketed under the trade name Resin 42-91 by the firm Ceca SA, Paris) and 60 g water were added to the stabile emulsion acidified in this manner under continuous stirring and the resultant mixture warmed to 55°C again with stirring, and then stirred for 4 hours at this temperature. After allowing it to cool to room temperature and adjusting the pH to 8.8 with 25% ammonium hydroxide a capsule dispersion resulted with capsules of approximately 3-8 micrometres diameter and a dry weight of approximately 38 per cent by weight.

The capsules are in the form of individual capsules with the associated advantages such as, for instance, advantageous redispersion of individual capsules in suitable dispersion agents.

Example 5

4 g of ferrous sulphate were added under stirring to a solution at room temperature, derived by mixing 211.5 g of water and 40 g of a 41% aqueous solution of a modified anionic melamine-formaldehyde precondensate (derived according to example 1 above), and the pH adjusted to approximately 3.6 with 20% H₂SO₄. To this solution was added 417.3 g of oil phase at approximately 42°C under stirring with a high-performance dispersion apparatus, the said oil phase comprising 156.5 g of chlorinated paraffin and 252 g of kerosene, as well as a total of 8.8 g of colour-forming agent. The colour-forming agent was a mixture of 75% crystal violet acetone and 25% 9-N-butyl-carbazolyl-(3)-4,4"-bis-(N-methyl-,N-phenylamino)-diphenylmethane. The resultant emulsion had a droplet diameter of approximately 3 to 10 micrometres which did not change significantly during the subsequent process steps.

The system was adjusted to a pH of approximately 3.0 by addition of 10 ml of 20% aqueous formic acid under gentle stirring. To this was added 131 g of an aqueous solution of non-ionic melamine-formaldehyde precondensate, comprising 80 g of the commercial product BC 336 (Bip, United Kingdom) and 51 g of water.

After warming of the emulsion to 58°C and maintenance at this temperature for 3.5 hours with gentle stirring, a capsule dispersion formed which, following cooling and neutralization with 25% ammonium hydroxide to a pH of 8, yielded capsules with a diameter of approximately 3 to 10 micrometres and the same properties as in Example 1. The dry matter content of the dispersion was approximately 47 per cent by weight.

Comparative example 1

Example 1 was repeated, but without the addition of acid to the sulphonated melamine-formaldehyde precondensate. Immediately after cessation of stirring with a high-performance dispersion apparatus, the emulsion disintegrated. The oil collected in part in pools on the fluid surface. It was not possible to produce capsules.



Claims

1. A method for the production of microcapsules through the microencapsulation of hydrophobic oils with substances dissolved or dispersed therein, especially colour reaction partners of colour reaction systems, whereby a hydrophobic oil containing the substance in dissolved or dispersed form is mixed with vigorous stirring with an aqueous medium, with the formation of aminoplast capsules in the resultant oil-in-water dispersion under acid conditions, the said aminoplast capsules subsequently isolated where desired, wherein at least one dispersion-stabilising compound which is not a reactive tenside is contained in the acid-adjusted oil-in-water dispersion, characterised in that the acidic oil-in-water dispersion contains A) a water-soluble anionic, sulphonated melamine-formaldehyde precondensate and/or B) a water-soluble anionic modified melamine-formaldehyde precondensate, and has been derived by
 - a) reacting, in a first step, melamine and formaldehyde at a temperature between 75 and 100°C in an alkaline medium in the presence of water with at least one compound (I) in the form of an alkali sulphite, an alkaline earth sulphite, an alkali sulphamate, an alkaline earth sulphamate, an aminosulphonic acid, an aminocarboxylic acid or an aminodicarboxylic acid, to form a precondensate
 - b) subsequently, in a second step, subjecting this precondensate to a polycondensation reaction at a pH of approximately 5.5 to 7.0 by rendering it acidic through the addition of at least one acidic compound (II) in the form of sulphamic acid, an aminocarboxylic acid, an aminodicarboxylic acid, a hydroxycarboxylic acid, a polyhydroxycarboxylic acid or an aminosulphonic acid, and
 - c) once the polycondensation reaction is complete, rendering the resultant resin solution alkaline through the addition, if necessary, of at least one basic compound (III), and
 - d) incorporating this, if necessary alkaline, resin solution for stabilization of the dispersion into the method, whereby the compounds A) and B) alone act to stabilise the dispersion and no water-soluble cationic compound is used for stabilization of the dispersion.
2. A method according to claim 1, characterised in that the water-soluble, anionic, sulphonated melamine-formaldehyde precondensate has on average approximately 0.7 to 1.3 sulphonate groups per melamine ring.
3. A method according to either claim 1 or 2, characterised in that the water-soluble, anionic, sulphonated melamine-formaldehyde precondensate has on average approximately 2 to 4 methylol groups per melamine ring.
4. A method according to at least one of claims 1 to 3, characterised in that the molecular weight of the water-soluble, anionic, sulphonated melamine-formaldehyde precondensate is in the range from approximately 3000 to 300,000.
5. A method according to claim 4, characterised in that the molecular weight of the



water-soluble, anionic, sulphonated melamine-formaldehyde precondensate lies between approximately 5000 to 100,000.

6. A method according to at least one of claims 1 to 5, characterised in that the water-soluble, anionic, sulphonated melamine-formaldehyde precondensate is contained in the aqueous medium at a concentration of approximately 0.3 to 25 per cent by weight.
7. A method according to claim 1, characterised in that to yield the water-soluble, anionic, modified melamine-formaldehyde precondensate, the melamine, the formaldehyde and the compound (I) are present in the first step in a molar ratio of approximately (1:3.5) to (6:0.5) to 1.
8. A method according to either claim 1 or 7, characterised in that the first step is performed at a pH of approximately 9.0 to 13.0.
9. A method according to at least one of claims 1, 7 and 8, characterised in that in the second step, the precondensate from the first step and the compounds from group II are present in a molar ratio of 1:0.1 to 3 with respect to the melamine used in the first step.
10. A method according to at least one of claims 1 and 7 to 9, characterised in that in the second condensation step, a mixture of sulphamic acid and glutamic acid, especially a mixture of equal parts of sulphamic acid and glutamic acid, is used as the group (II) compound.
11. A method according to at least one of claims 1 and 7 to 10, characterised in that the second step is carried out at a temperature of approximately 75 to 100°C.
12. A method according to at least one of claims 1 and 7 to 11, characterised in that the basic compound (III) is in the form of an alkali hydroxide, an alkaline earth oxide, an alkaline earth hydroxide, an amine, a polyamine, monoethanolamine, diethanolamine, triethanolamine and/or a basic metal compound.
13. A method according to at least one of the foregoing claims, characterised in that additional metal compounds in the form of salts of bivalent or multivalent metals are contained in the oil-in-water dispersion.
14. A method according to claim 13, characterised in that the metals are calcium, magnesium, aluminium, iron, zinc, nickel, cobalt, manganese, titanium, zircon and/or silicon.
15. A method according to at least one of claims 1 to 14, characterised in that a water-soluble, non-ionogenic melamine-formaldehyde precondensate is used to form the aminoplast capsules.



16. A method according to claim 13, characterised in that a melamine-formaldehyde precondensate, partially etherified with methanol, is used as the water-soluble, non-ionogenic melamine-formaldehyde precondensate.
17. A method according to at least one of claims 1 to 14, characterised in that urea-formaldehyde precondensates are used to form the aminoplast capsules.
18. A method according to at least one of claims 1 to 14, characterised in that mixtures of melamine-formaldehyde precondensates and urea-formaldehyde precondensates are used to form the aminoplast capsules.
19. A method according to at least one of the foregoing claims, characterised in that other aminoplast-forming compounds, such as aldehyde-precondensates based on thiourea, N-alkylurea, guanidine, acetoguanamine, benzoguanamine, caprinoguanamine, cyanamide, dicyandiamide and alkyl/arylsulphonamide, are used to form the aminoplast capsules in addition to melamine-formaldehyde precondensates and urea-formaldehyde precondensates.
20. A method according to at least one of claims 1 to 19, characterised in that a further water-soluble, anionic sulphonated melamine-formaldehyde precondensate or a compound B) is added to the aqueous reaction system to reduce its viscosity.
21. A method according to at least one of the foregoing claims, characterised in that the colour reaction partner of a colour reaction system is dissolved or dispersed in the hydrophobic oil to be encapsulated.