

EUROPEAN QUALIFYING EXAMINATION 1994

PAPER A CHEMISTRY

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INSTRUCTIONS TO CANDIDATES

You are to assume that you have received the annexed letter from your client including a description of an invention for which he wishes you to obtain a European patent together with references to the most pertinent prior art known to your client.

You should accept the facts given in the paper and base your answers upon such facts. Whether and to what extent these facts are used is your responsibility.

You should not use any special knowledge you may have of the subject-matter of the invention, but are to assume that the prior art given is in fact exhaustive.

Your task is to draft an independent claim (or claims) offering the applicant the broadest protection possible while at the same time having a good chance of succeeding before the EPO. In drafting your claim(s) you should bear in mind the need for inventive step over the prior art indicated, the requirements of the Convention, in particular as to the form of claims, and the recommendations made in the Guidelines for Examination in the EPO. Dependent claims should also be drafted so as to enable you to fall back upon them should the independent claim(s) fail and should be kept to a reasonable number.

You are also expected to draft an introduction, i.e. that part of the description which precedes the examples or the explanation of the drawings. The introduction should be sufficient to provide support for the independent claim(s). In particular, you should consider the advisability of mentioning advantages of the invention in the introduction.

You are expected to draft claims and an introduction for one European patent application only. This application should meet the requirements of the Convention as to unity. If you would in practice seek to protect further inventions by filing one or more separate applications, you should, in a note, clearly identify the subject-matter of the independent claim of such separate application(s). However, it is not necessary to draft the wording of the independent claim for the or each separate application.

In addition to your chosen solution, you may – but this is not mandatory – give, in a note, the reasons for your choice of solution, for example, why you selected a particular form of claim, a particular feature for an independent claim, a particular piece of prior art as starting point or why you rejected or preferred some piece of prior art. Any such note should however be brief.

It is assumed that you have studied the examination paper in the language in which you have given your answer. If this is not so, please indicate on the front page of your answer in which language you have studied the examination paper. This always applies to candidates who – after having filed such a request when enrolling for the examination – give their answer in a language other than German, English or French.

Different sets of claims for those states which have made reservations under Article 167 (2) EPC are not required.

PAPER A/1994 (Chemistry)

Client's letter

I work in the food industry, and together with a chemist who is a friend of mine, I am investigating various possibilities of manufacturing foods with a low caloric value, in line with the general trend towards "healthier" eating and the use of slimming products.

In this context we have come across a group of compounds which can be employed for various purposes as emulsifiers or foaming agents. With the help of these compounds products of varying texture, ranging from creamy, slightly expanded substances suitable for use as spreads, to products resembling highly foamed whipped cream can be prepared. The compounds can be used, for example, to make a butter substitute. The properties of such products are significantly influenced by the emulsifiers or foaming agents used. The subject which particularly interests me is the use of these compounds to prepare a kind of ice-cream substitute. My friend, however, seeks to obtain a more general form of protection, his view being that the compounds are in themselves new and have a wide variety of potential applications in other fields as well as the food industry. The compounds in question are certain esters of glycerine derivatives with a range of fatty acids.

The common feature of these products, which are normally based on aqueous emulsions, is that they have a significantly lower caloric value than their conventional equivalents. This is because the compounds we have found make it possible, for example, to reduce the proportion of fatty ingredients, or indeed to eliminate such ingredients altogether, while taking account of the need to avoid impairing taste and other pleasant oral sensations (mouthfeel).

We feel that the time has now come to seek patent protection for our invention, and we would therefore ask you to take the necessary steps to obtain a European patent on our behalf.

Our invention does not only relate to the esters themselves; we have also devised what we think is an unusual method of preparing them, together with a particularly elegant way of processing them.

Our glycerol esters have 3 to 10 glycerol units linked to each other by ether groups in a polyglycerol chain. One or more of the hydroxyl groups in the polyglycerol can be esterified with saturated or unsaturated straight-chain fatty acid residues. Suitable fatty acids range from straight-chain carboxylic acids with a total of 12 carbon atoms (lauric acid) to those with a total of 26 carbon atoms (cerotic acid) and include those with 14 (myristic acid), 16 (palmitic acid), 18 (stearic acid) and 20 (arachidic acid) carbon atoms. These can be used to prepare compounds which are completely water-soluble or compounds which are completely oil-soluble.

The compounds suitable for our purposes proved to be those with one or two fatty acid ester groups, preferably those which are not water-soluble but show good water-dispersability. With the palmitic and arachidic esters we obtained particularly stable emulsions which lend themselves well to further processing and can be foamed. The stearates are even better suited to our purposes. Here, special mention is made of hexaglycerol distearate and decaglycerol distearate. The best product of all is triglycerol monostearate.

The process we used to produce these esters consists in converting the relevant polyglycerol with an ester of the chosen straight-chain fatty acid in the

presence of fatty acid soap and a catalyst. Methyl esters, or esters with another alcohol boiling at up to about 100°C are particularly suitable.

Almost any fatty acid soap can be used for the process, provided that a certain proportion of it has a fatty acid chain length of less than 15 carbon atoms. This proportion should be at least 8% by weight of the total amount of the fatty acids bound in the soap. Soaps with a very short chain length (6 carbon atoms or more) may be used, but best results are obtained using soaps with a chain length of 10 to 12 carbon atoms.

The molar ratio between the reactants is also very important. The ratio of soap to polyol must be between 0.1:1 and 2.5:1; with regard to yield and reaction time, the optimum ratio is approximately 1.6:1. The ratio of ester to polyol must be between 10:1 and 20:1.

Any of the normal catalysts for this type of reaction may be used; for example, any strong base, such as sodium or potassium hydroxide, may be used. Solvents can also be used. The pressure is adjusted so that the low-boiling alcohol released during the reaction can be removed by distillation. The temperature is normally maintained within the range of 100 to 180°C, preferably within the range of 110 to 150°C.

Once the polyglycerol esters have been prepared, they have to be converted into a usable form. The problem is that they have a wax-like consistency which makes it difficult to blend them.

One known process for handling wax-like compounds involves blending them in a molten state - at a temperature above their melting-point, e.g. at least 70°C - with some of the other solid ingredients with which they are to be further processed. Another known method of processing wax-like products is to grind the deep-frozen materials to a powder at temperatures ensuring that they remain sufficiently brittle. However, during this grinding the process conditions must be controlled in a very complicated and costly way and the grinder often becomes clogged.

We have found it a better way instead to pass the molten ester through a spray dryer operated with cold air (at a temperature of less than 30°C) as a cooling medium, so that, on emerging from the spray nozzle, the material solidifies into fine particles. As in the case of the grinding method, other ingredients may be added at this point to prevent the fine particles from sticking together.

The polyglycerol ester has a sufficient emulsifying effect in amounts of at least 0.3% by weight. The texture of the resultant emulsion varies according to the amount of the ester. If the concentration exceeds 5% by weight, the product takes on a fatty, butter-like consistency, even if whipped with air. In the course of our experiments we found that a concentration of 2 to 5% by weight of the polyglycerol ester yields a mix, which does not resemble butter and which can be foamed to provide a high degree of expansion and is suitable for use as a topping resembling whipped cream. The amount of expansion is determined by the extent of whipping or mixing.

For this purpose a suitable amount of hot water and the other ingredients are added to the polyglycerol ester and so much air is beaten into the mixture with a mechanical mixer (an ordinary household electric mixer will do) that the resultant foam does not expand any further. The temperature of the water is not particularly important: it can be anywhere within the range of 50 to 100°C.

However, to improve the texture of the mixture, the temperature at the time of whipping must be between 50 and 60°C, preferably between 52 and 57°C.

Other ingredients may also be added: for example, fats, flavouring, colouring and bodying agents, such as milk powder, whey powder, dried egg, sugar or artificial sweetener. Dextran is an example of a suitable bodying agent, if a very low caloric value is desired.

The fully expanded foam products collapse after a short time unless a hydrophilic vegetable gum is added as a foam stabiliser, in an amount ranging from 0.2 to 3.5% by weight of the aqueous phase. Gum arabic (acacia gum), xanthan gum, guar gum or carrageenan are particularly suitable. However, it must be remembered that vegetable gums tend to inhibit foaming or even prevent it altogether. When preparing fully expanded foams (e.g. for toppings), the gums can therefore only be added after the foam has developed. The resultant mixture is smooth and substantially tasteless.

After numerous unsuccessful attempts we found that for frozen desserts such as ice-cream, the amount of bodying agents and the amount of the above-mentioned non-aqueous ingredients altogether should not exceed, respectively, 45 and 55% per cent by weight of the total mixture. Thereto our polyglycerol ester (0.5-1% by weight of the total) and water are added. Blending and whipping are adjusted to provide a 0.5 to 1.1-fold expansion (a so-called overrun of 50 to 110%), thereby obtaining a stable emulsion with good mouthfeel.

As well as acting as a stabiliser, the vegetable gum also improves the texture of the final product. For example, it delays or prevents unwanted crystallisation of ice or sugar. For frozen desserts, a liquid melt is desired. Excess stabiliser prevents this and leads to the formation of a stiff, pudding-like melt - a phenomenon known as "melt resistance". In the present case, the amount of stabiliser is therefore limited to between 0.2 and 0.5% by weight.

In the course of further experiments, my friend has found that the process described above is also suitable for producing other esters on the basis of polyols. These polyols evidently need to have at least 3 hydroxyl groups. As far as chain length is concerned, the only requirement seems to be that the fatty acids be in a liquid state at the reaction temperature. However, the method is best suited to the esters cited above.

If I am correctly informed, it is advisable to give examples illustrating the invention. I therefore include the following description of experiments, taken from my friend's lab journal.

Step 1: 690 g (7.5 mol) of glycerol and 6 g of KOH were charged under nitrogen in a flask with a mechanical mixer and heated to about 260°C until approximately 90 g of water had distilled off. The yellow viscous oil was then dissolved in distilled water, treated with a little activated charcoal and filtered off. The water was removed by distillation. A virtually colourless and odourless triglycerol was obtained.

Step 2(a): 18 g (75 mmol) of the triglycerol obtained in step 1 was dissolved in a beaker at room temperature with 1.05 g of 85% KOH solution (16 mmol KOH) and 25 ml of water.

Step 2(b): 314 g (approximately 1060 mmol) of methyl ester of soybean oil fatty acids (>95% by weight, C₁₄ to C₂₀) was combined with 20.8 g (approximately 120 mmol) of a commercial mixture of fatty acids (mainly having a chain length of 10

carbon atoms). The resultant mix was then neutralised with an aqueous solution of 85% KOH (120 mmol KOH).

Step 3: The solutions from Steps 2(a) and 2(b) were mixed at a temperature of 60°C and a pressure of 3 mbar (3hPa). These conditions were maintained constant for 30 minutes. Conversion to a mixture of triglycerol mono- and di(soybean oil fatty acid) esters was almost complete. The product was washed several times with an aqueous soda solution and isopropyl alcohol. Further purification was carried out by extraction and steam distillation. The resultant solid was melted and passed through a spray dryer into air having a temperature of 25°C. By this means, a finely comminuted product was obtained which stored well for an extended period at temperatures below 30°C.

In the following example, 8g of triglycerol monostearate was dispersed in 8g of water and kept at 52-57°C overnight. On the next day, the following additives and water were added to this dispersion to provide a total of 1000g:

Skim milk solids	166.2 g
Sugar	184.9 g
Guar gum	2.0 g
Carrageenan	1.0 g
Polysorbate 80	0.4 g
Water	629.5 g

The mix was then pasteurised at 74°C for 20 seconds. Flavours and colours having a total weight of 2 g were added, and the mixture was homogenised and loaded into a commercial soft-serve ice-cream freezer. The freezer was adjusted to provide for 60% overrun. An extremely light-textured ice-cream was obtained.

Almost identical results were achieved using hexaglycerol distearate and decaglycerol diarachidinate. However, the texture of the foam was not so fine, and with the arachidic ester the foam was somewhat coarser than with the distearate.

For example, we prepared a calorie-reduced concentrate for toppings using 46 parts by weight of sucrose (sugar), 25 parts by weight of a hydrogenated coconut oil and 5 parts by weight of a triglycerol monoester with fatty acid derived from dehydrated castor oil (mainly octadecadienic acids, $C_{18}H_{30}COOH$), with 24 parts by weight of water. The sugar and emulsifier were combined and then dispersed in the water at a temperature of 45°C. The hydrogenated oil was then added in a high-speed mixer.

The concentrate was added to the same amount by weight of cold milk and whipped for 3 minutes at 5°C in a household mixer running at maximum speed to achieve a 5 to 6-fold expansion. One part by weight of gum arabic was then carefully worked into the mixture. The product had a pleasant texture with good mouthfeel and flavour. It was suitable for use as a stiff, stable "cream" topping.

You will probably also be interested to see what we have found in literature. I therefore enclose the relevant documents.

DOCUMENT I (State of the Art)

Recent amendments to the legislation governing food, drugs and cosmetics have imposed strict limits on the use of emulsifiers in the food industry. Due to recent results in research many of the emulsifiers which were widely employed in the past may now only be used in very small quantities. These formerly popular emulsifiers include esters of sugar alcohols and their polyethoxylated derivatives, for example, the polyoxyethylene sorbitan esters, which are now only allowed in extremely low concentrations because they are not broken down in the body but they must be excreted or they are possibly deposited in certain organs in the body. They may give rise to cumulative effects.

Under these circumstances there was a need for physiologically acceptable water-soluble emulsifiers with broad applicability. We have identified a class of polyglycerol esters which largely meets these requirements. These compounds are obtained from polyglycerols and fatty acids having a relatively short chain-length which are bound to one or more hydroxyl groups of the glycerol component. We have investigated a number of these compounds and found that water-solubility is insufficient if at least two of the following conditions apply: short polyglycerol chains, long-chain fatty acids, and/or high rates of esterification.

The polyglycerols have 4 to 12 hydroxyl groups, depending on the number of glycerol units which can be between 2 and 10. In theory, therefore, the number of fatty acids bound to the polyglycerols can be between 1 and 12. Combinations of different fatty acids can be used.

The compounds which we investigated included tetraglycerol monoctanoate and decaglycerol tetrahexanoate, to mention two specific compounds.

DOCUMENT II (State of the Art)

The invention relates to a food product comprising a shelf-stable emulsion with a low caloric value, prepared with the following ingredients (proportions by weight):

0.1 to 1 parts neutral fat
1 part water
1 to 2 parts dextran
6 to 8% (relative to the total weight of the emulsion) of polyglycerol fatty acid esters serving as emulsifiers, and flavouring and colouring or combinations thereof.

Food products with a low caloric value have repeatedly been prepared in the past. However, the results of these experiments have always lacked the necessary shelf-stability which is especially important for industrial use. For example, an edible emulsion comprising sorbitan monostearate, sugar and water has been disclosed, but it was found that after only a short period of storage at room temperature, an emulsion of this type takes on the stiff consistency of a non-spreadable shortening.

Other known preparations showed better storage-stability but were highly viscous and had an objectionable flavour, owing to the fact that they contained a high proportion of potassium oleate - i.e., a soap.

As well as being appreciably more stable, the present product has excellent spreading properties; it also shows good resistance to microbial spoilage and is void of any soapy flavour.

Example

A stable aqueous emulsion was prepared using a mixture of polyglycerol esters as an emulsifier. The emulsion concentrate was made up of 20% fat, 25% water, 49% dextran and 6% emulsifier. A quantity of butter colour and flavour was added.

The emulsion concentrate was prepared by blending all the ingredients except the water, which was subsequently added at a temperature of 85°C. The mixture was stored for 24 hours at room temperature and mechanically whipped to obtain a slightly expanded butter-like spread.