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(71) **Applicant** *(for all designated States except US)*: **AJKAI TIMFÖLD KFT.** [HU/HU]; Gyártelep, H-8401 Ajka (HU).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **FEJES, Pál** [HU/HU]; Kelemen u.8, H-6720 Szeged (HU). **KIRICSI, Imre** [HU/HU]; Hobiart basa u. 18/b, H-6723 Szeged (HU). **VARGA, Károly** [HU/HU]; Budakeszi út 49/b, H-1021 Budapest (HU). **KISS, Éva** [HU/HU]; Hargitai u. 56/b, H-6726 Szeged (HU). **BAKSA, György** [HU/HU]; Újélet u. 14/d, H-8400 Ajka (HU). **BALOGH, Zoltán** [HU/HU]; Tűzoltó u. 5., H-8400 Ajka (HU). **VALLÓ, Ferenc** [HU/HU]; Újélet u. 12., H-8400 Ajka (HU). **SITKEI, Ferenc** [HU/HU]; Újélet u. 18 A/4, H-8400 Ajka (HU). **NAGY, Ivánné** [HU/HU]; Széchenyi u. 124., H-8400 Ajka (HU). **TÓTHNÉ, Gyutai, Mariann** [HU/HU]; Ujvilág u. 55, H-8400 Ajka (HU). **GRÉLINGER, Gábor** [HU/HU]; Újélet u. 6., H-8400 Ajka (HU). **MAGYAR, János** [HU/HU]; Ifjúság u. 2/E, H-8400 Ajka (HU).

(74) **Agent: INTERINNO PATENT OFFICE**; Margit krt. 73., H-1024 Budapest (HU).

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(54) **Title:** A METHOD FOR PRODUCING SYNTHETIC ZEOLITES WITH ENLARGED GRAIN SIZE AND ZEOLITES WITH ENLARGED GRAIN SIZE PRODUCED BY THE SAID METHOD

(57) **Abstract:** A process for producing synthetic NaA, NaX, NaY zeolites or their mixtures comprising: a gel is prepared by means of mixing together intensively a mixture of sodium aluminate solution, water-glass solution and water (solution 'A'), a mixture of water-glass solution and water (solution 'B') and intensive stirring of synthesis nuclei solution formed by intensive mixing together of solutions 'A' and 'B', the formed gel is crystallized with a slow stirring up to the moment of the highest crystallization rate (t_{infl}), then a crystal size growing gel, free of synthesis nuclei and having mole ratio limits identical with initial gel is added in one or several portions and the crystallization proceeds with a slow stirring, and if required, the addition of the crystal size growing gel and the following crystallization are once or more times repeated, thereafter the obtained crystals are separated, washed and dried by a known method.

A METHOD FOR PRODUCING SYNTHETIC ZEOLITES WITH ENLARGED GRAIN SIZE AND ZEOLITES WITH ENLARGED GRAIN SIZE PRODUCED BY THE SAID METHOD

The subject of invention is a method for producing synthetic NaA, NaX; NaY zeolites or their compositions with enlarged grain size.

Furthermore, the subjects of invention are zeolites, as well as compositions of zeolites produced by the above mentioned method.

The zeolites with enlarged grain size according to invention have advantages in the usage, like enhanced tenside seizing ability and more homogenous distribution of grain size.

It is well-known, that both natural zeolites and artificial ones crystallize out spontaneously. According to Breck's manual (E. D. W. Breck: "Zeolite Molecular Sieves", J. Wiley, 1974), it is possible to form 17 types of zeolites in the quaternary system consisting of components SiO_2, Al_2O_3, Na_2O and H_2O.

They don't crystallize out at a well-defined composition, but at a variety of compositions within a more or less wide range thereof, which are usually delineated in ternary composition diagrams (at fixed temperature and H_2O content) (see p. 270 of the referred Breck's manual)

In the figure 1 the field or range is marked with scattered points wherein the NaA is able to crystallize anyway, at the composition corresponding to a defined point of the ternary composition field on the base of 1 mole of Al_2O_3 at the values of $H_2O \cong 94$ moles and $T \cong 88C°$.

Methods for producing a NaA zeolite is described in the Hungarian patent specification of Registry No. 198 892 and in the US patent specifications of Registry Nos. 4 222 995, 4 303 627, 4 303 628, 4 305 916, furthermore in the German Federal Republic documents laid open to public inspection (Auslegeschrift) of Registry Nos. 2 651 419, 2 651 420, 2 651 436, 2 651 437, 2 651 278.

In the said diagram the nucleus formation is quick within the area T, it is significantly slower and sustained in the time at the point B and the spontaneous nucleus formation is practically absent at the point C.

It is generally true, that the tendency to nucleus formation increases by increase of quantity of the component facilitating the gel dissolution (actually Na_2O) under unchanged other conditions.

The composition of the crystalline (zeolite) phase, also most typically the Si/Al proportion can change within a certain range, being typical for the structure within a type of zeolite (having identical radiographic structure, like FAU = faujasite, MFI = ZSM-5 etc.), and eventually, if a variant with the possible highest Si/Al proportion (with the highest thermal stability, as result thereof) should be produced keeping a defined structure, the concentration of alkaline reagent must be reduced to such a degree that the ability of spontaneous crystallization is completely lost.

The same occurs, if the aluminum silicate is dissolved not under influence of alkaline agent but by complex formation e. g. under influence of ions F^-.

It results from the above mentioned that nucleus formation and gel crystallization should be separated in space and time during the synthesis of artificial zeolites.

This procedure is unavoidable in certain cases and expedient in other ones.

Without fulfilling this condition the crystalline phase could be namely produced as radiographically pure one only with high difficulties or not at all.

The homogeneity of the zeolite phase should be assured, however not in any case.

For some specific purposes (e. g. softening of wash water) in several industrial applications (e. g. detergent production) not one but two types of zeolites can be utilized, so it does not result in any disadvantage, if not one but two phases crystallize (NaA[LTA] and NaX[FAU] according to the mentioned example) simultaneously from the sludge.

The promotion of the crystallization is well-known from a number of patents using aging of gels, insertion of crystalline nuclei, as well as inoculation with different crystalline nuclei.

To promote crystallization of NaX and NaY, nuclei were produced by means of aging of gels, according to Breck's original patent dated 1964 (US patent No. 3 130 007) and according to US patents of Registration

Nos. 3 518 051 and 3 227 660, as well. The US patent of Registration No. 4 264 562 deals with nucleus formation.

According to US patent of Registration No. 4 016 246 "the activation of Na-metasilicate" is performed using addition of Al_2O_3 to metasilicate.

The methods described in US patents of Registration Nos. 3 071 434 and 3 322 272 utilize NaA, NaX and NaY produced by synthesis as crystallization nuclei.

According to US patent of Registration No. 4 404 823 NaX nuclei are used to produce NaA and NaX simultaneously.

The crystallization of zeolite is promoted by nuclei with significantly larger surface (their size is ~0.1-0.01 μm) according to US patent of Registration No. 4 166 099.

Crystallization nuclei are described in the German documents laid open to public inspection (Auslegeschrift) of Registry No 2 447 206.

In the US patents of Registration Nos. 4 178 352 and 4 340 573 a rigid gel suspended in water is used as nuclei and moreover "Al nuclei" are used according to the latter one for crystallization of NaA.

The aging of gels and the addition of used silicate component to Al_2O_3 of 50 to 2000 ppm used in the above cited procedures are difficult to reproduce and control under industrial conditions (because the commercially available water-glass always contains this quantity of Al_2O_3 contamination).

The "diluted" in water rigid gels have an irreproducible structure and they can lead to difficulties during the large-sized production of zeolites.

The same relates to the other heterodispersive previously crystallized agents, and it should be added, that the diverse dispersiveness will be transmitted to the inoculated product, too.

A large-scale separation by sedimentation or by any other method requires a great expenditure.

In relation to the "nuclei" several requirements should be fulfilled.

I.) The first requirement is that the production of nuclei should be reproducible both in laboratory and in large-scale environment with a relative divergence of at least ± 20 %. Since the nucleus formatting agents of gel structure and the more or less crystalline agents cannot be reproduced with such high accuracy, the "solution of nuclei" (this "solution" contains in fact particles of colloidal size, of less than 50 nm) should be mainly considered or preferred.

(This recognition encouraged us to develop a former invention containing $N = 4.4\ (\pm 0.9) * 10^{11}$ crystallization nuclei per gram).

II.) The quantity of nuclei N should be enough to "suppress" "inhibit" the eventual formation of parasitic zeolite nuclei by educing the components formed in the watery (generally in solvent) phase, being necessary to build up crystal grating.

The fulfillment of this condition is highly dependent on the structure of the zeolite to be crystallized:

- the NaA zeolite is "undemanding" in this aspect. A quantity of nuclei of $0.1*N\ (g^{-1})$ is surely enough and $0.01*N\ (g^{-1})$ is even assumably enough to control properly the crystallization of NaA in a sludge composition appropriate to formation of NaA.

We recognized, that the same "nuclei solution" is applicable to crystallize NaA, NaX or NaY.

This means, that nuclei of NaA, NaX and NaY are the same.

This is the raison why the phase NaA (LTA) always appears depending on the composition of sludge and the conditions of crystallization during crystallization of low modulus zeolite X ("low silica X", LSX) product, as well.

It does not make any disadvantage in applications for detergent production, since both zeolites have their own destinations.

(The NaA removes ions of calcium, the LSX removes ions of magnesium from wash-water.)

The same nuclei crystallize out as NaA on abundance of aluminum or as NaX (as well as NaY) zeolite on abundance of silicate.

Consequently no "Al-nucleus" is required, which was proposed in the US patent specification of Registry No. 4 340 573.

III.) The added nuclei must grow to a zeolite product having an optimal for usage grain size Φ (μm) and homogenous distribution thereof in a charge of sludge of defined quantity.

There are some independent conditions in addition to described in II.) ones the accomplishment thereof is not initially assured.

Three cases can occur:

- The quantity of nuclei N (g^{-1}) contained in a mass unit of the nuclei solution can be changed within a certain range at a defined mass of charge so that the condition II) will be fulfilled.

  During this procedure a product having grain size within an interval ($\Phi_{min.}$ to $\Phi_{max.}$).

  If the required grain size Φ is within the interval ($\Phi_{min.}$ to $\Phi_{max.}$) the grain size of the product can be enlarged slightly reducing the quantity of the nuclei solution added to the charge for the synthesis and the grain size of the product can be reduced slightly increasing the quantity thereof, consequently the conditions II) and III) are simultaneously fulfilled.

- If the required grain size Φ is smaller than $\Phi_{min.}$, the quantity of the nuclei solution added to the defined charge can be increased.

- It is usual for the majority of cases that the required grain size Φ is greater than $\Phi_{max.}$, consequently the number of nuclei N (g^{-1}) relating to the defined charge should be reduced, but it cannot be done because the condition II) would not be fulfilled and in this case another zeolite of undesired type would be crystallized out of parasitic nuclei.

The present invention provides a relatively simple procedure to fulfill simultaneously the conditions II) and III) and complying with the requirement to enable the production of a zeolite of any previously defined grain size Φ within the range of 1 to 20 μm preferably in the practically required range of grain size of 3 to 8 μm.

Based on this recognition, our invention relates to the intended, previously defined enlargement of grain size of synthetic zeolites, having the essential point to add a nucleus-free gel to the sludge to be crystallized, expediently at a time t_{infl}, and in the quantity required to produce the previously defined grain size Φ in such a manner that the highest rate of crystallization being characteristic for the given conditions should remain unchanged during the whole time period of addition.

It is the necessary condition thereto to have a sludge to be inoculated with nuclei of a composition unable to build up nuclei spontaneously.

The sludge complying with said condition (gel solution phase) is inoculated with a nuclei solution fulfilling the condition II) or the sludge is made up with a water-glass solution, which contains the concentration of nuclei assuring the fulfillment of condition II).

This water-glass solution is always doped with aluminum silicate (with content of 1 mole of Al_2O_3 rated to 8 to 15 mole of SiO_2) and it is highly alkaline with a concentration of free NaOH of 16 to 24 weight %.

The nuclei formation is quick under these conditions (it takes only a few hours).

According to invention the charging can be performed in any succession.

It is more expedient, however, to add water-glass to the ready gel.

Thereafter the sludge is warmed up to the temperature of crystallization and the crystallization begins.

A zeolite product with too small grain size should be received without intervention.

A quantity of sludge being free of crystallization nuclei is charged into crystallizing apparatus at a defined phase of crystallization according to the rate calculated to zeolite type to be crystallized and to the desired grain size Φ_1.

Having terminated it the crystallization is continued up to the safe crystallization of the last portion of the charged sludge.

It is essential to define the time of gel addition.

The crystallization rate is described by the differential equation

$$\frac{dm}{dt} = C_1 f(c) F \tag{1}$$

where:

m (g) - is the mass of zeolite (of a grain or a given number of grains);

f(c) - is a function containing the concentration of aluminum silicate components *(c)* required to build up the crystal grating

$F(m^2)$ - is the surface of the crystal to the solution

While the gel of adequate quantity is present, *f(c)*= cons., so it can be involved into C_1.

The differential equation (1) provides a solution as third-degree polynomial function of time for any form of crystal:

$$m = C_0 + C_1^{\prime} + C_2^{\prime 2} + C_3^{\prime 3} \tag{2}$$

being an increasing convex function of t.

As time is progressing, the gel runs down neither the *f(c) = cons.* is fulfilled any more, nor the equation (2) as consequence.

The convex character of the function changes to concave in the moment $t_{infl.}$

dm/dt decreases and tends towards zero, the function *m(t)* tends to a constant limit by increasing the time, as it is shown in the figure 2.

The charge of nuclei free gel should be begun expediently at the moment t_{infl} and proceed according to the defined program in the time to maintain the optimal crystallization rate.

It is expedient to charge continuously the gel.

The charge rate (g/s) should be adequate that mass ratio of zeolite building components be equal to (*dm/dt*) i. e. the zeolite building rate.

Looking at the equation (2) one can recognize that *dm/dt* is a square function of time, consequently the charge rate should be evenly accelerating to assure the optimum of crystallization.

It is expedient to charge the gel at an evenly accelerating rate by this reason.

However, this condition cannot be exactly fulfilled by technical reasons, it can be approximated quite well by various solutions.

The whole quantity of subsequently charged gel is determined by the desirable grain size Φ (μm). It can be calculated, but it is preferably defined experimentally for the purposes of a safe production.

The said principles can be applied to a zeolite of any type with reasonable adaptations.

The product obtained by the method according to invention can be significantly more homogeneous, than by any other method, wherein the nucleus building is accomplished with dragging.

It appeared as unexpected result, that the radiographic long time order of the products NaA and NaX crystallized with usage of nuclei is higher than the other samples produced without nuclei addition, this fact was manifested that intensity of reflections appearing at great angles 2Θ (net planes of high index) is unexpectedly increased.

We suppose that transporting processes accomplish quicker in a structure free of sliding and other dislocations, which can influence advantageously the speed of adsorption and the catalytic activity (for NaY zeolite), as well.

This fact has a great importance even in the several times mentioned detergent production application, because the procedure of ion-exchange is also accelerated in a structure being free of grating defects and the wash-water becomes quicker “soft ”.

The execution of the procedure according to invention has the feature that a sludge containing components SiO_2, Al_2O_3, Na_2O and H_2O and nuclei of crystallization is crystallized during the time t_{infl}, until the conditions of highest crystallization rate are established, then a sludge containing components SiO_2, Al_2O_3, Na_2O and H_2O and free of crystallization nuclei is charged continuously to the crystallized mixture, until the crystals grow up to the desired average size.

As it is mentioned above, the procedure according to the present invention is applicable to produce a number of different zeolites. Not only zeolites NaA and NaX, but also NaY zeolite and their mixtures can be produced by the above mentioned procedure, as well.

The procedure proves to be peculiarly advantageous for producing of NaX zeolite or mixture of NaX and NaA ones in industrial viewpoint.

According to one of the variants of this invention NaX zeolite of modulus m≅2.0 to 5.3 can be produced advantageously at pH = 13.2 and with enlargement of average grain size in several grades, using production and addition of crystallization nuclei.

Among the conditions it is emphasized that the pH value of the sludge cannot exceed 13.2 because a spontaneous nuclei formation begins at 13.3 to 13.4 and the addition of nuclei becomes useless.

The procedure resulting in formation of zeolite with grain size of $\Phi > 1$ to 2 μm consists of the following actions:

- Execution of the first synthesis up to the moment t_{infl} resulting in the formation of product with grain size of Φ_1
- execution of the second synthesis starting from the moment t_{infl} providing product with grain size Φ_2.
- execution of the third synthesis providing product with grain size
  Φ_3, which can vary between 3 and 10 μm.

The required addition of crystallization nuclei is determined by molar ratios of components SiO_2, Al_2O_3 and H_2O of the sludge used for the first synthesis.

To assure a pH value never exceeding 13.2 of the first sludge, the following molar ratios should be kept:

$SiO_2/Al_2O_3 = 1.5$ to 5.3

$Na_2O/Al_2O_3 = 1.5$ to 2.5

$H_2O/Al_2O_3 = 88$ to 260

Should be undesired that the effect of nuclei addition were disturbed by spontaneous nuclei formation, the sludge used for following syntheses should have similar molar ratios.

During the following experiments we came to the result that the said target can be easily reached without any production and addition of crystallization nuclei. Consequently, the second variant, the variant (b) of the procedure according to invention consists in producing a zeolite NaX or a mixture of zeolites NaA and NaX of moduluses m = 2.5 to 5.3 of average grain size Φ > 2 μm. Zeolite NaY can also be produced by the same way.

It is not necessary to produce and add crystallization nuclei at augmented concentration of alkali.

The procedure consists of the following steps:

- Water-glass, aluminate alkali, solution of NaOH and distilled water are mixed together, so the solution 'A' i. e. the first sludge of synthesis is produced;
- Initiation of the crystallization process;
- Base solutions of water-glass, aluminate alkali, solution of NaOH and distilled water are mixed together to produce solution 'C', the second sludge of synthesis;
- Addition of solution 'C' to the solution or gel 'A' being in process of crystallization;
- completion of crystallization;
- Filtrating, washing and drying of crystals.

It is essential to add solution 'C' made up of the same components as the 'A' one at the adequate moment t_{infl} after the beginning of crystallization of 'A', because this assures to form zeolites NaA and NaX of adequate grain sizes and to avoid the formation of other undesired zeolites: P zeolite, phillipsite, sodalite etc. The molar ratios of components of the solution 'A' calculated to 1 mole of Al_2O_3 are within the following ranges:

$SiO_2/Al_2O_3 = 2$ to 5.3

$Na_2O/Al_2O_3 = 2.5$ to 7.5

$H_2O/Al_2O_3 = 88$ to 260

The molar ratios of the solution 'C' have much wider ranges, because the spontaneous nuclei formation makes no disturbance.

The proportions of components SiO_2, Al_2O_3, Na_2O, H_2O calculated to 1 mole of Al_2O_3 are as follows:

$SiO_2/Al_2O_3 = 2$ to 100

$Na_2O/Al_2O_3 = 2.5$ to 100

H_2O/Al_2O_3 = 88 to 5000

The size of crystals being formed can be controlled very well by choosing the moment of addition of solution 'C'.

It is advisable to define previously the adequate moment t_{infl} by means of experiments.

Having the target to produce a zeolite with average grain size of 5 to 8 μm, solution 'C' should be added 1 to 2 hours after the beginning of crystallization of the solution 'A'.

On addition of the solution 'C' to the one 'A' being in crystallization later, 3 to 24 hours after the beginning of crystallization, the zeolite crystals can grow up to the average grain size Φ = 15 to 30 μm.

Consequently, the subject of invention is a procedure to produce synthetic NaA, NaX, NaY zeolites or their mixtures from solutions of sodium aluminate and water-glass.

The features of procedure according to invention are as follows:

(a)

A gel is produced, having the composition:

1.5 to 5.3 moles of SiO_2/1 mole of Al_2O_3,

1.5 to 2.5 moles of Na_2O/1 mole of Al_2O_3,

88 to 260 moles of H_2O/1 mole of Al_2O_3

and pH = 13.2 at the highest by making a mixture of sodium aluminate solution, water-glass solution and water (solution 'A'); and a mixture of water-glass solution and water (solution 'B'), then mixing intensively together the solutions 'A' and 'B' to obtain a solution of synthesis nuclei. The gel obtained by this way is crystallized during a slow stirring up to the moment when the highest crystallization rate is achieved (t_{infl}), then a gel of the same molar ratio, free of crystallization nuclei, serving to growing up the crystal size is added in one or several portions to the primary one and the crystallization is continued during slow stirring, the addition of gel for growing up the crystal size and following crystallization can be one or more times repeated if desired, then the obtained crystals are separated, washed and dried by known methods; or

(b)

a solution 'A' of pH = 13.3 at least of the composition

2.0 to 5.3 moles of SiO_2/1 mole of Al_2O_3,

2.5 to 7.5 moles of Na_2O/1 mole of Al_2O_3,

88 to 260 moles of H_2O/1 mole of Al_2O_3

is made by intensive mixing together of sodium aluminate solution, water-glass solution and the resulting gel is crystallized up to the moment when the highest crystallization rate is reached, then a solution 'C' of the composition

2.0 to 100 moles of SiO_2/1 mole of Al_2O_3,

2.5 to 100 moles of Na_2O/1 mole of Al_2O_3,

88 to 5000 moles of H_2O/1 mole of Al_2O_3

obtained by mixing intensively together of sodium aluminate solution, water-glass solution and distilled water is added in one or more portions to the mixture containing crystals and the following one or more steps of crystallization are continued up to reaching the desired crystal size and the produced crystals are separated, washed and dried by known methods.

Furthermore, the subjects of this invention are NaA, NaX and NaY zeolites or their composition produced by the above mentioned method having the feature that the average particle size is at least 1.0 μm, expediently between 1.0 and 20.0 μm.

The zeolites of enlarged grain size according to invention can be applied on wide application field.

Furthermore, the advantages of zeolites produced according to invention are as follows:

The most adequate product can be used on a specific field of application owing to conscious setting of average grain size.

The distribution of grain size is more uniform than in case of zeolites produced by a traditional method.

The method and products according to invention are introduced by the following examples.

Example 1

NaX zeolite is produced with modulus m ≅ 2.6 (Si/Al = 1.3), at a pH value about 13.1 so that the average grain size reaches approximately $\Phi = 3$ in three steps.

Production of synthesis nuclei

Two solutions marked by 'A' and 'B' respectively are made as follows.

Making solution 'A'

53.4 g of solid NaOH (containing 87 weight % of NaOH) is dissolved in 137.0 g of H_2O. This solution id distributed in mass proportion 1 to 1 to 14.1 g of aluminate alkali having molar ratio 1.58 Na_2O/Al_2O_3 and NaOH concentration of 15.9 weight % and 77.4 g of water-glass solution having concentrations of Na_2O of 8.6 weight % and of SiO_2 of 28.0 weight %.

The solutions of aluminate and water-glass diluted as mentioned above are warmed up to 40 $C^0$and under intensive stirring are poured together, then it is stirred for 5 minutes more and kept during 70 minutes at the temperature of 40.0 ± 2 C^0.

(A small amount of flocculated deposit can be formed which dissolves during heat treatment.)

This homogenous solution can be stored for at least a week in refrigerator.

To improve the storage ability at room temperature it can be mixed with water-glass solution 'B'.

Preparation of solution 'B'

500 g of water-glass solution having concentrations of Na_2O of 8.6 weight % and of SiO_2 of 28.0 weight % is diluted with 350 g of H_2O.

The solution 'A' is added during intensive stirring to the solution 'B'.

This mixture is named hereinafter "nuclei".

The composition of this "nuclei" is: (96.6 SiO_2, 1.0 Al_2O_3, 49.8 Na_2O, 1858.0 H_2O).

A quantity of 1 g of said "nuclei" contains $4.3 * 10^{11}$ with relative deviation of ± 5 % NaX and NaA nuclei of grain size less than 5 nm (having not particularized structure).

Execution of the first synthesis

2000.0 g of H_2O and 432.2 g of "nuclei" are added to 1542.9 g of water-glass solution of concentrations of Na_2O of 8.6 weight % and of SiO_2 of 28 weight % and the resulting solution is kept.

3670.0 g of H_2O is added to 1362 g of aluminate alkali of molar ratio 1.58 Na_2O/Al_2O_3 having concentration of Na of 15.9 weight %.

The solutions are mixed together under intensive shearing stirring and simultaneous addition of both solutions.

A gel is obtained as result.

The gel is stirred thereafter during 15 minutes more.

The pH value measured after completion of stirring is 13.2.

This gel is crystallized under a slow stirring without shearing force at temperature of 88 ± 2 C^0 samples are taken in regular time periods for X-ray diffraction analysis, the results of measurements make up the crystallization diagram shown in the Figure 2.

The molar ratios are as follows:

SiO_2	Al_2O_3	Na_2O	H_2O
2.99	1.0	2.489	165.27

The X-ray diffraction is proportional to the mass of crystalline phase being present in the volume of given sample.

The ordinates of Figure 2 show "eö" the summarized intensity of the net plains having the most intensive reflection of indices [111], [220], [535], [642]/[646], [555], [157]/[751] as function of sampling time.

A good result can also be obtained, when measurements are performed only with reflection [555]/[157]/[751] appearing at about $2\ \Theta = 30.9^0$ (half measurement width * height).

One can read out of the diagram made from crystallization data of several charges that the crystallization terminates after 5.5 to 6.0 hours (if this unique charge should be crystallized).

The time corresponding to the inflection point is: t_{infl}=3.2 hours.

After a crystallization of 6 hours the product is filtrated, washed with hot distilled water until the pH = 10.5 is reached, then dried at 100 C^0 in air flow and finally stored above saturated solution of NH_4Cl.

The proportion of Si/Al using atom adsorption system (AAS) is defined as: Si/Al= 1.36, the modulus is: m=2.782

The composition of a primary cell is:

$Na_{81}[AlO_2)_{81}(SiO_2)_{111}]\sim 260\ H_2O$ which differs only by 5 to 6 % from that of a NaX cell considered as typical:

$$Na_{86}[AlO_2)_{86}(SiO_2)_{106}]\sim 264\ H_2O$$

The theoretic output can be determined on the base that the whole quantity of Al_2O_3 is transferred into product (with a close approximation).

The mass of zeolite containing 1 mole of Al_2O_3 shall be:

$$2.27\ SiO_2\ 1.0\ Al_2O_3\ 1.0\ Na_2O\ 6.4\ H_2O = 442.6\ g$$

The theoretically expectable output (of the above mentioned charge) is: 2.655*442.6 = 1175.1 g.

The mass of sludge to be crystallized is: 9056.0 g (for the above charge, too).

Consequently, $\Phi = 1175.1/9056 = 0.130$ g zeolite crystallizes out of a unit mass of sludge (13.0 %).

(We took several samples out of the crystallizing system, we did not test the output by this reason).

The integral chart of grain size distribution of the product determined by sedimentation method is reproduced on the Figure 3, one can read therefrom that the average grain size is: $\Phi = 1.45$ µm.

The diffractogram of zeolite made by α radiation of copper K is represented on the Figure 4. It is remarkable, how the reflections after $2\Theta \cong 23^0$ (of the page [533] at $2\Theta \cong 23.5^0$, the reflection of [642]/[246] at 20 to 26.9^0, that of page [555]/[157] at $2\Theta \cong 31.2^0$) are intensive, which indicates to a durable order.

Should be the expectable grain size of $\Phi = 1.45$ µm achieved in the present experiment unsatisfactory, the crystallization should be continued after 3.2 hours at the second stage.

The charge 1 reaches its highest crystallization rate at this moment.

This rate will be reduced after this moment because of the diminution of gel quantity (i. e. the quantity of so-called secondary components being present in the solution diminishes, what is reckoned with by function f(c)). It can be prevented by proceeding to the step 1 c) of the procedure.

Execution of the second synthesis

The addition of gel having the "substantially identical" composition begins at the crystallization time $t_{infl} \cong 3.2$ hours to increase the grain size.

This gel, however, must not contain crystallization nuclei.

The gel of following composition is loaded into crystallization vessel in uniform portions during 1.5 hours.

1763.3 g of water-glass having concentrations of 8.6 weight % of Na_2O and 28.0 weight % of SiO_2 is diluted with 2600.0 g of H_2O.

1362.7 g aluminate alkali having mass concentration of 15.9 % and molar ratio of 1.58 Na_2O/Al_2O_3 is diluted with 2807.7 g H_2O.

The two solutions are mixed together at a desirable lower temperature (but at least at room-temperature) with intensive stirring.

The formed gel is used without aging.

The composition of the gel is as follows:

SiO_2	**Al_2O_3**	**Na_2O**	**H_2O (moles)**
3.00	1.0	2.409	156.33

The absolute time is 3.2 + 1.5 = 4.7 hours at the completion of addition.

Should be continued the crystallization up to the 7th hour in , a product of crystallization degree according to 1 b) will be produced, as it seems from the diffractogram on the Figure 5.

Reading off from the diagram of integral grain size distribution one finds the average grain size $\Phi = 2.45$ μm.

Having defined by method AAS Si/Al = 32 and the modulus is m = 2.64.

The composition of basic cells is:

$Na_{83}[Al_2O_3)_{83} (SiO_2)_{109}] - 260 H_2O$

so the difference is only 3.6 % from the NaX composition considered as typical.

The mass of above described charge is 8584.4 g and at most 1158.0 g zeolite can be produced therefrom.

Should be considered the grain size of Φ = 2.45 µm to be still too small, one can proceed to the step of "third synthesis" in the 7th hour (continuing the calculation in absolute time).

Execution of the third synthesis

The gel used for second synthesis is made in double quantity (it weights 17168.8 g),

This gel is added in a similar manner, beginning from the 7th hour during 1.5 hours to the sludge being in the crystallization vessel.

The crystallization is continued under a slow stirring up to the end of 10th hour.

The crystals are filtrated, washed and dried as in the previous procedures.

The diffractogram presented on the Figure 7 shows an excellent crystal quality too.

The Figures 4 and 7 are almost identical.

The proportion of Si/Al remained practically unchanged as defined by method AAS (Si/Al = 1.31).

The diagram of integral grain size distribution is shown on the Figure 8.

Φ = 3.2 µm.

On the base of the above described examples, the following questions can be answered:

i.) How much gel should be charged totally to obtain a previously defined grain size Φ (defined in grams or how many "mass units" of charge is necessary).

ii.) what addition rate should be kept to assure the optimal crystallization rate.

Zeolite NaX (as well as NaY) crystallizes out in form of more or less distorted octahedral crystals, having edge length as characteristic "size".

The devices based on the principle of sedimentation and used for determination of integral "grain size distribution" perform selection, however, not according to edge length but according to sedimentation speed.

It should not cause an excessive distortion if the crystal size gained by the usage of sedimentation principle are considered as the same for both octahedral and hexahedral crystals.

Obviously, there is a relationship between the mass of zeolite m = g) being either a single crystal or a multitude of crystals of approximately the same size and the crystal size Φ (defined advantageously in μm) as follows:

$$\Phi = c_1 \sqrt[3]{m}$$

Should be considered the mass of the "charge of mass unit" as unit of m, the average grain size Φ can be also considered as function of quantity of charges.

It is known that $\Phi_1 = 1.45$ μm at m = 1 so according to (3)

$c_1 = 1.45$

for m = 2

$\Phi = 1.45 * \sqrt[3]{2} = 1.83$ μm

for m = 3

$\Phi = 1.45 * \sqrt[3]{3} = 2.09$ μm

for m = 4

$\Phi = 1.45 * \sqrt[3]{4} = 3.20$ μm

A continuous curve was drawn through these calculated points on the Figure 9.

The experimental values are denoted by *o*-s (where the value pertaining to m = 1 was the basic point).

The values of Φ measured experimentally (by means of sedimentation method) are higher than the calculated ones, but the diminishing characteristic of the measured increments $\Delta\Phi$ confirms the function according to $\sqrt[3]{m}$.

The absence of accurate accordance can originate from the different definition of the "geometrical dimensions" and "sedimentation dimensions", but supposedly the crystallizing sludge is in fact not completely homogenous after all and it even partially recrystallizes during crystallization.

Furthermore, crystals clump partially because of the absence of shearing (which explains the long-continued "tail" of the sedimentation curve) and, as electron micrographs show, even geminate crystals can be formed by epitaxial growth.

To determinate m to the chosen Φ, it is the most adequate way to reckon with function (3), take data of laboratory measurements as base and interpolate according to theoretical relationship (m can be, of course a real value too).

To produce a $\Phi = 2.0$ μm, $m \cong 0.4$ "charge unit" ($0.4*8548.4 \cong 3419.4$ g of sludge), to reach $\Phi = 3.0$ μm $m \cong 2.2$ "charge unit" ($2.2*8548.4 \cong 19661.3$ g of sludge) must be added to the first charge.

The function (2) describing the change of zeolite mass in the time means at the same time, that the characteristic grain size Φ is linear function of time:

$$\Phi = A_0 + t \cong A_1 t_1 (i.e.\, d\Phi / dt = A_1 = const.) \qquad (4)$$

whereas if $t \to 0$ $\Phi \to 0$ (i. e. the size of "nuclei" are ignored).

If the deceleration should not occur because of diminution of gel quantity, the crystal size could reach the size $\Phi = 4.48$ μm in the sludge being analogous to the first charge even after 4.28 hours according to the crystallization diagram of the Figure 2, consequently

$$A_1 = \frac{1.45}{4.28} \cong 0.339\, \mu m / hour$$

the crystallization time concerning to the size $\Phi = 3.2$ μm is 7.2 hours (in case of an unlimited growth) according to (4).

A proportionality exists between the size Φ and the mass m (where m can be both the mass of a unique crystal and that of any nearly homogeneously disperse conglomerate) as follows:

$$m \sim \Phi^3 = A_1^3 t^3 = B\,t^3$$

$m \cong 1175.1$ g within the time $t_1 = 4.28$ hours (in case of unlimited growth), consequently

$$B = \frac{1175.1}{t_1^3} = \frac{1175.1}{(4.37)^3} = \frac{1165.1}{78.40} \cong 15.0$$

that is

$$m = 15 * t^3$$

furthermore

$$\frac{dm}{dt} = 45.0 * t^2$$

We could reach practically about 70 % of this rate only.

One can calculate by the formula

$$\frac{dm}{dt} \cong 32.4 * t^2$$

Using the notation M for the mass of gel, a simple relation

$$\frac{1dm}{\sigma dt} = \frac{dM}{dt} = \frac{32.4t^2}{0.135} \cong 240t^2$$

can be established between $dm/_{dt}$ and the rate of addition of gel $dM/_{dt}$.

Consequently, the gel should be added by a growing rate t^2 to maintain the optimal crystallization rate.

This condition cannot be accomplished by the majority of existing pumps.

$dM/_{dt}$ is reproduced as function of t on the basic diagram 10.

The area under the curve i. e. the integral of $dM/_{dt}$ from t = 3.2 hours to t = 7.2 hours is identical to the mass of three "charge units" (3*8584.4 g = = 25753.2 g).

If only one pumping speed was used, this feeding can be accomplished by the speed of

$$w_o = \frac{dM}{dt} = \frac{25753.2}{(7.2-3.2)} = 6438.2 \text{ g/hour}$$

It is allowed, however, to use a feeding speed less than w_o during the first two hours and a feeding speed more than w_o during the second two hours.

If the diagram $dM(t)/_{dt}$ expressed exactly the circumstances, the time of addition could be calculated easily for two defined pumping rate.

Nevertheless, the diagram is only approximately exact, the pumping rate should be chosen $w_1 = 4200$ g/hour (the mass of charged gel is 8400 g) for the first two hours and the rest quantity of 17353 g should be charged by rate of

$$w_2 = \frac{17353.2g}{2} = 8676.6 \text{ g/hour}$$

that is approximately twice faster during one hour by this reason.

The feeding rate can be easily doubled by using two pumps.

This principle explains the approximately doubled addition rate according to (3).

Example 2

We show in this example, that the growing of grain size is also realizable in the synthesis of zeolite NaA(LTA).

To produce the gel 600.0 g of H_2O and 179.6 g of water-glass solution having concentrations of 8.6 weight % of Na_2O and 28.0 weight % of SiO_2 are added to 432.2 g of "nuclei" solution and the mixture is stirred up intensively.

512.2 g of aluminate alkali having molar ratio of 1.58 Na_2O/Al_2O_3 and NaOH concentration of 15.9 weight % is diluted with 647.5 g of water in another vessel.

The gel is produced by uniting the homogenized solutions at a possible lower temperature (but at least approximately at room temperature) and intensive stirring up.

The gel can be stirred hardly in the first minutes, but after 5 to 10 minutes the stirring goes well.

The gel has pH = 13.04 (measured with a calibrated pH meter).

The molar ratios of the components of gel are as follows:

SiO_2	Al_2O_3	Na_2O	H_2O (moles)
1.8	1.01	2.317	112.71

The gel is poured into a crystallizing vessel and crystallized under an intensive shear stress at 88 ± 2 C^0.

The first four reflections of X-ray diffractogram of the product (at the net planes of indices [200], [220], [222] and [420] are shown on the Figure 12.

From the integral sedimentation diagram of the Figure 13 one can read out that
$\Phi = 1.60\ \mu m$

The proportion of Si/Al determined by method AAS is: Si/Al = 1.05.

The inflection point of the crystallization graph is: t_{infl} = 55 to 60 min.

Production of gel for growing up the crystal size

A gel free of crystallization nuclei is produced.

500.0 g of H_2O is added to 400 g of water glass solution having concentrations of 8.6 weight % of Na_2O and 28.0 weight % of SiO_2.

527.9 g of H_2O is added to 512.2 g of aluminate alkali having molar ratio of
1.58 Na_2O/Al_2O_3 and concentration of 15.9 weight % of NaOH.

A homogenous gel is produced from the previously homogenized solutions by mixing them together under intensive shear stress.

The molar ratios are as follows:

SiO_2	Al_2O_3	Na_2O	H_2O (moles)
1.8	1.0	2.078	92.26

Execution of the synthesis

The gel is crystallized up to $t_{infl} \cong 55$ to 60 minutes during the first synthesis, then the whole gel quantity necessary for the growing of crystalline grain size is added along 1.5 hours.

The product is filtrated, washed up to pH $\cong$ 10.5 washed with hot water and dried.

It is stored above saturated solution of NH_4Cl.

The first four diffractograms of the product is shown on the Figure 14, which indicates that crystallization degree of the product is excellent.

The average grain size is: Φ = 4.1 μm as it is read form the integral sedimentation graph of the Figure 15.

It can be established, that growing of grain size of NaA zeolite can be resolved by this method. The dependence of size Φ on the number of charges differs from that of NaX which is mainly structural habit, but the composition variables are also different.

Our further experiments resulted that this target can be reached easily without separate nuclei production and addition thereof, too.

Example 3

The target is to produce a mixture of NaA-NaX zeolites of average grain size of Φ = 8 to 9 μm and high seizing abilities for tensides and good seizing abilities for CaO and MgO ions.

Preparation of solution 'A', initiation of the crystallization

4800 g of water-glass solution having concentrations of 8.9 weight % of Na_2O and 28.1 weight % of SiO_2 is mixed together with 4850 g of H_2O and 1000 g of NaOH solution of concentration of 45.17 weight % in a vessel.

9000 g of aluminate alkali of molar ratio 1.5 Na_2O/Al_2O_3 and concentration of 15.8 weight % is mixed together with 4850 g H_2O and 1000 g of NaOH solution having concentration of 45.17 weight % in another vessel.

Then the two solutions are mixed together with intensive stirring and the crystallization is initiated at 25 C^0.

The molar ratios are as follows:

SiO_2	**Al_2O_3**	**Na_2O**	**H_2O (moles)**
2.64	1.0	3.65	114.74

Preparation of solution 'C'

1493 g of water-glass solution having concentrations of 8.9 weight % of Na_2O and 28.1 weight % of SiO_2 is mixed together with 177 g of solid NaOH dissolved in 360 g of H_2O in a vessel.

433 g of aluminate alkali of molar ratio 1.5 Na_2O/Al_2O_3 and concentration of Na of 15.8 weight % is mixed together with 177 g of solid NaOH dissolved in 360 g of H_2O in another vessel.

Finally the two solutions are mixed together with intensive stirring and the solution 'C' is obtained with the following molar ratios:

SiO_2	**Al_2O_3**	**Na_2O**	**H_2O (moles)**
13.63	1.0	14.31	224.91

Execution of crystallization:

The solution 'C' is added to the solution 'A' having been crystallizing since 1 hour with an intensive stirring and the temperature is raised to 60 C^0.

After 3 hours the temperature is raised to 80 C^0 and the crystallization proceeds for 6 hours with slow stirring.

Filtrating and washing

The zeolite crystals are filtrated with suction filter and washed with condensation water up to pH < 10.

The composition of the obtained product:

Parameter	**Measured value**	**Method of measurement**
NaX %	91	XRD PW 1710
NaA %	9	XRD PW 1710
Molar ratio SiO_2/Al_2O_3	2.37	Gravimetry, titration
Ion exchange capacity of CaO mg/g	138	Complexometry
Ion exchange capacity of MgO mg/g	85	Complexometry
Average grain size Φ μm	8.7	Laser diffraction, CILAS 1064
Tenside seizing ml/100 g	200	Modified standard DIN-ISO 787/5
BET m^2/g	47	GEMINI Z370

A zeolite skeleton formatting agent well applicable to modern washing powders is obtained.

Example 4

The target is to produce a X zeolite with high ability to seize tensides and good ability to seize CaO and MgO ions having average grain size $\Phi = 4$ to 6 μm and molar ratio of 2.45 SiO_2/Al_2O_3.

Preparation of solution 'A', initiation of crystallization:

4700 g of water-glass solution having concentrations of 8.9 weight % of Na_2O and 28.1 weight % of SiO_2 is mixed together with 5400 g of H_2O and 100 g of NaOH solution of 45.17 weight % in a vessel.

9500 g of aluminate alkali having molar ratio of 1.62 Na_2O/Al_2O_3 and NaOH concentration of 15.5 weight % is mixed together with 5400 g of H_2O and 100 g of NaOH solution of 45.17 weight %.

Then the two solutions are mixed together with intensive stirring and the crystallization is initiated at 25 C^0.

The molar ratios are as follows:

SiO_2	Al_2O_3	Na_2O	H_2O (moles)
2.63	1.0	2.77	127.66

Preparation of solution 'C'

1515 g of water-glass solution having concentrations of 8.9 weight % of Na_2O and 28.1 weight % of SiO_2 is mixed together with 113 g of solid NaOH dissolved in 1573 g H_2O in a vessel.

114 g of aluminate alkali having molar ration of 1.62 Na_2O/Al_2O_3 and concentration of NaOH of 15.5 weight % is mixed together with 112 g of solid NaOH dissolved in 1572 g of H_2O in another vessel.

Finally the two solutions are mixed together with intensive stirring and the solution 'C' is obtained.

The molar ratios are as follows:

SiO_2	**Al_2O_3**	**Na_2O**	**H_2O (moles)**
53.87	1.0	39.54	1788.93

Execution of crystallization:

The solution 'C' is added to the solution 'A' having been crystallizing since 1 hour with intensive stirring and the temperature is raised to 60 C^0.

After 3 hours the temperature is raised to 80 C^0 and the crystallization proceeds for 6 hours with slow stirring at this temperature.

Filtrating and washing

The sludge containing zeolite crystals is filtrated with suction filter and washed with condensation water until pH<10.

The composition of the obtained product is:

Parameter	**Measured value**	**Method of measurement**
NaX %	100	XRD PW 1710
Molar ratio SiO_2/Al_2O_3	2.45	Gravimetry, titration
Ion exchange capacity of CaO mg/g	132	Complexometry
Ion exchange capacity of MgO mg/g	69	Complexometry
Average grain size Φ μm	6.6	Laser diffraction, CILAS 1064
Tenside seizing ml/100 g	145	Modified standard DIN-ISO 787/5
BET m^2/g	6.5	GEMINI Z370

A zeolite well-applicable as modern molecular sieve is obtained.

Example 5

The target is to produce a mixture of NaA and NaX zeolites with good seizing capacity of CaO and MgO ions and average grain size of Φ = 15 to 20 μm.

Preparation of solution 'A', initiation of crystallization:

4700 g of water-glass solution having concentrations of Na_2O of 8.6 weight % and of SiO_2 of 27.4 weight % is mixed together with 4800 g of H_2O and 850 g of NaOH solution having concentration of NaOH of 45.17 weight % in a vessel.

10200 g of aluminate alkali having molar ratio of 1.65 of Na_2O/Al_2O_3 and concentration of NaOH of 15.05 weight % is mixed together with 4800 g of H_2O and 850 g of solution of NaOH having concentration of 45.17 weight % in another vessel.

Then the two solutions are mixed together with intensive stirring and the crystallization is initiated at 30 C^0.

The molar ratios are as follows:

SiO_2	Al_2O_3	Na_2O	H_2O (moles)
2.63	1.0	3.71	120.45

Preparation of solution 'C':

2070 g of water-glass solution having concentrations of Na_2O of 8.6 weight % and of SiO_2 of 27.4 weight % is mixed together with 245 g of solid NaOH dissolved in 500 g of H_2O in a vessel.

600 g of aluminate alkali having molar ratio of 1.65 Na_2O/Al_2O_3 and concentration of NaOH of 15.05 weight % is mixed together with 245 g of solid NaOH dissolved in 500 g of H_2O in another vessel.

Finally the two solutions are mixed together with intensive stirring and the solution 'C' is obtained.

The molar ratios are as follows:

SiO_2	Al_2O_3	Na_2O	H_2O (moles)
15.0887	1.0	16.01	257.899

Execution of crystallization:

20 % of the solution 'C' is added to the solution 'A' having been crystallizing since 1 hour with intensive stirring, then the crystallization proceeds.

80 % of the solution 'C' is added to the previous solution in the second hour of crystallization with intensive stirring and the temperature is raised to 60 C^0.

After 3 hours the temperature is raised to 80 C^0 and the crystallization proceeds for 6 hours with slow stirring at this temperature.

Filtrating and washing

The sludge containing zeolite crystals is filtrated with suction filter and washed with condensation water until pH<10.

The composition of the obtained product is:

Parameter	**Measured value**	**Method of measurement**
NaX %	68	XRD PW 1710
NaA %	31	XRD PW 1710
Molar ratio SiO_2/Al_2O_3	2.28	Gravimetry, titration
Ion exchange capacity of CaO mg/g	47.3	Complexometry
Ion exchange capacity of MgO mg/g	80.2	Complexometry
Average grain size Φ μm	17.9	Laser diffraction, CILAS 1064
Tenside seizing ml/100 g	125	Modified standard DIN-ISO 787/5
BET m^2/g	18	GEMINI Z370

A special zeolite well-applicable as gross grained molecular sieve is obtained.

CLAIMS

1. A procedure for producing synthetic NaA, NaX, NaY zeolites or their mixtures from solutions of sodium aluminate and water-glass, with characteristics that

(a) a gel of composition of:

1.5 to 5.3 moles of SiO_2/1 mole of Al_2O_3,
1.5 to 2.5 moles of Na_2O/1 mole of Al_2O_3,
88 to 260 moles of H_2O/1 mole of Al_2O_3
having at most pH = 13.2

is prepared by means of mixing together intensively a mixture of sodium aluminate solution, water-glass solution and water (solution 'A'), a mixture of water-glass solution and water (solution 'B') and intensive stirring of synthesis nuclei solution formed by intensive mixing together of solutions 'A' and 'B', the formed gel is crystallized with a slow stirring up to the moment of the highest crystallization rate (t_{infl}), then a crystal size growing gel, free of synthesis nuclei and having mole ratio limits identical with initial gel is added in one or several portions and the crystallization proceeds with a slow stirring, and if required, the addition of the crystal size growing gel and the following crystallization are once or more times repeated, thereafter the obtained crystals are separated, washed and dried by a known method. or

(b) a solution 'A' of composition of

2.0 to 5.3 moles of SiO_2/1 mole of Al_2O_3,
2.5 to 7.5 moles of Na_2O/1 mole of Al_2O_3,
88 to 260 moles of H_2O/1 mole of Al_2O_3
having at least pH = 13.3

is prepared by means of intensive mixing together sodium aluminate solution, water-glass solution and water, the formed gel is crystallized with slow stirring until the moment of the highest crystallization rate is reached, then a solution 'C' of the composition of:

2.0 to 100 moles of SiO_2/1 mole of Al_2O_3, 2.5 to 100 moles of Na_2O/1 mole of Al_2O_3 and

88 to 5000 moles of H_2O/1 mole of Al_2O_3

formed by intensive mixing together of sodium aluminate solution, water-glass solution and distilled water is added in one or several portions to the mixture containing crystals, and the following step or several steps of crystallization are continued until the desired crystal size is reached, the produced crystals are separated, washed and dried by known methods.

2. The variant (a) of the procedure according to Claim 1 with characteristics that the crystal size growing gel is added continuously by a uniformly accelerating rate in the time.

3. The variant (a) of the procedure according to Claim 1 with characteristics that the crystallization is executed at the temperature of 88 ± 2 C^0.

4. The variant (b) of the procedure according to Claim 1 with characteristics that the first step of the crystallization is executed at the temperature of 22 to 30 C^0, the following step thereof is executed at the temperature of 60 to 80 C^0.

5. The variant (b) of the procedure according to Claim 1 with characteristics that the solution 'C' is added in one portion.

6. The variant (b) of the procedure according to Claim 1 with characteristics that the solution 'C' is added in several portions.

7. Synthetic zeolites or a mixture thereof produced according to variants (a) or (b) of Claim 1 with characteristics that the average particle size of zeolites is at least 1.0 µm, preferably 1.0 to 20.0 µm.

8. The zeolites or their mixtures according to Claim 7. with characteristics that the average particle size of zeolites is 3.2 µm.

9. The zeolites or their mixtures according to Claim 7. with characteristics that the average particle size of zeolites is 8.7 µm.

10. The zeolites or their mixtures according to Claim 7. with characteristics that the average particle size of zeolites is 17.9 µm.

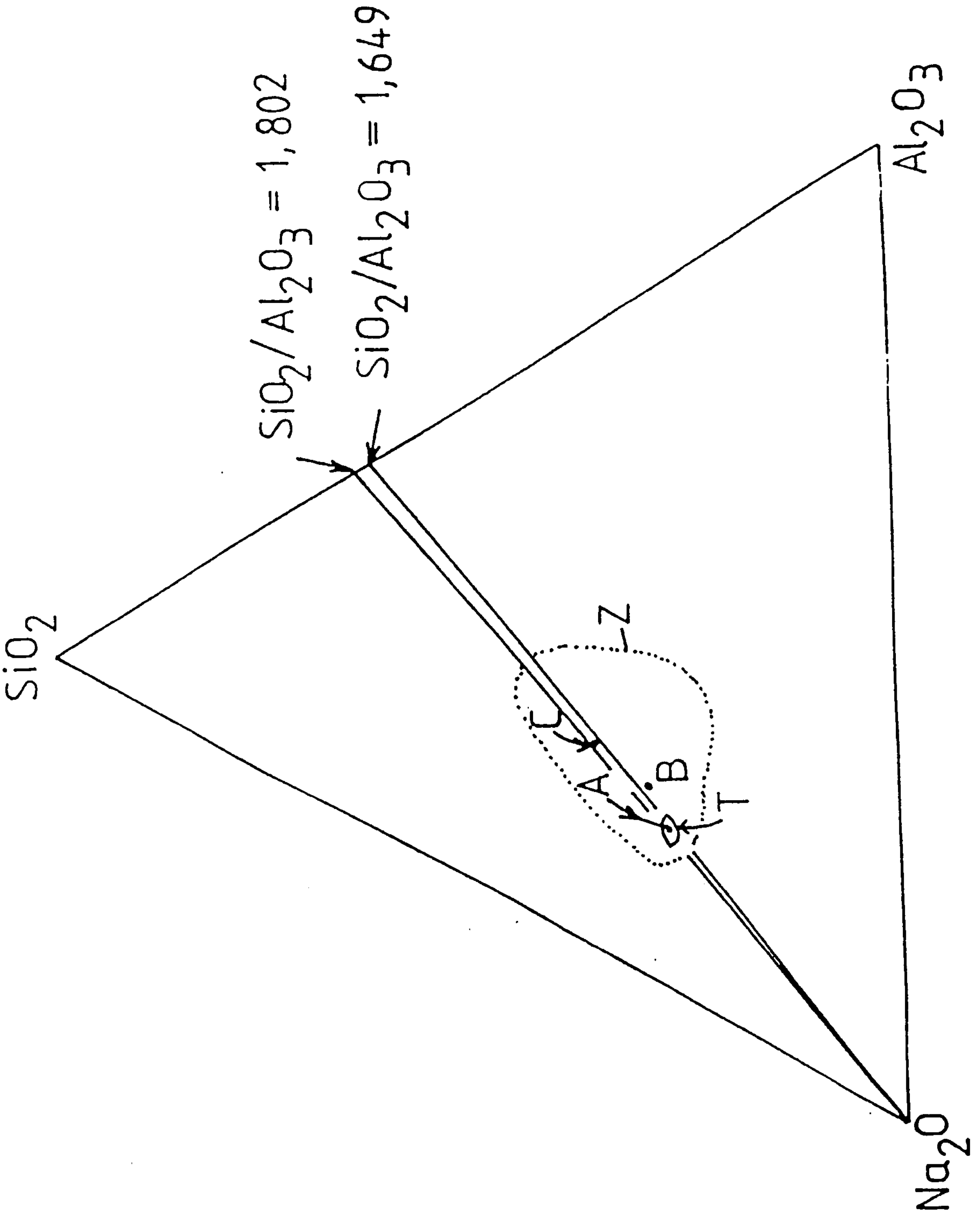

FIG. 1.

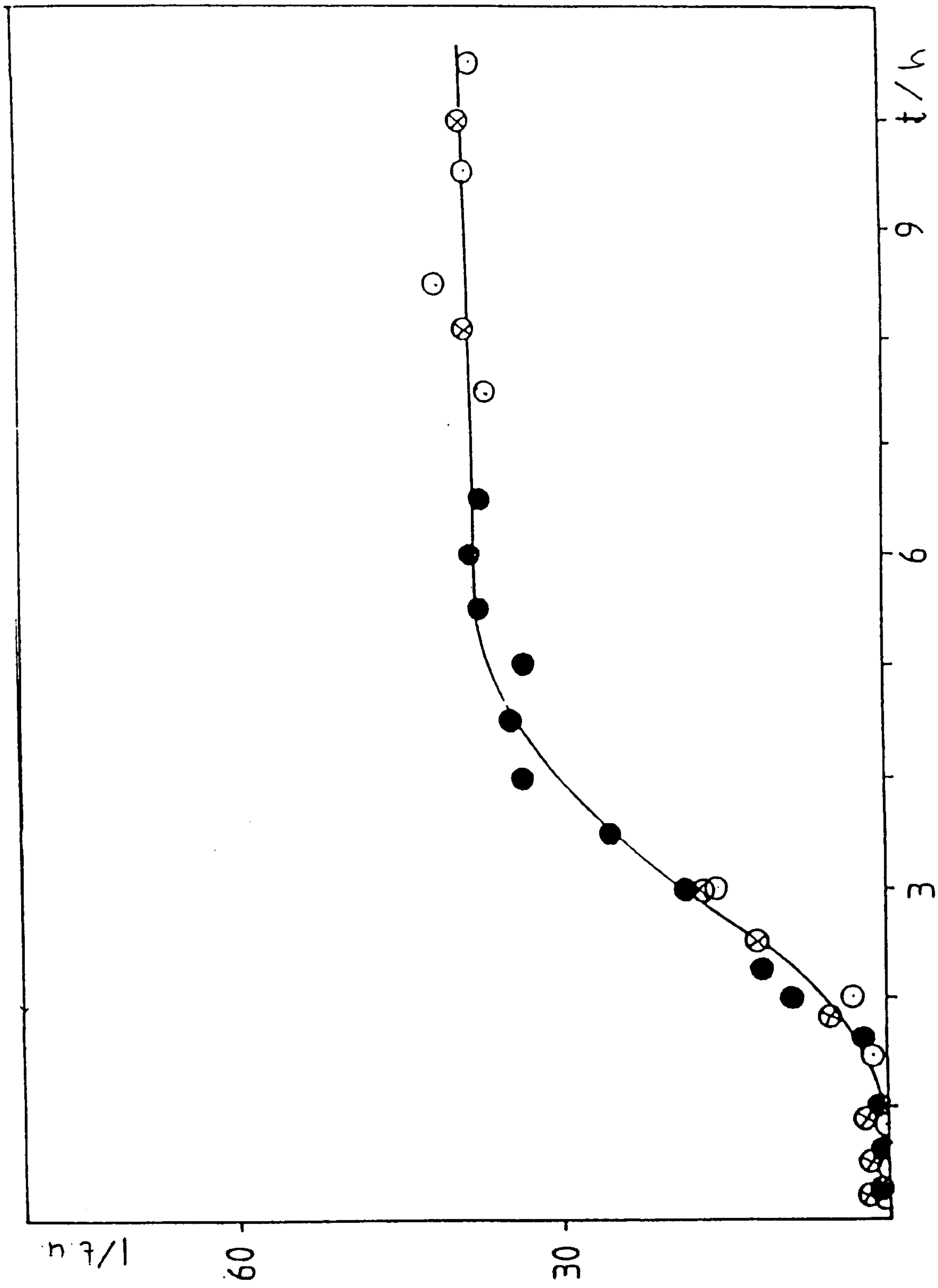

FIG. 2.

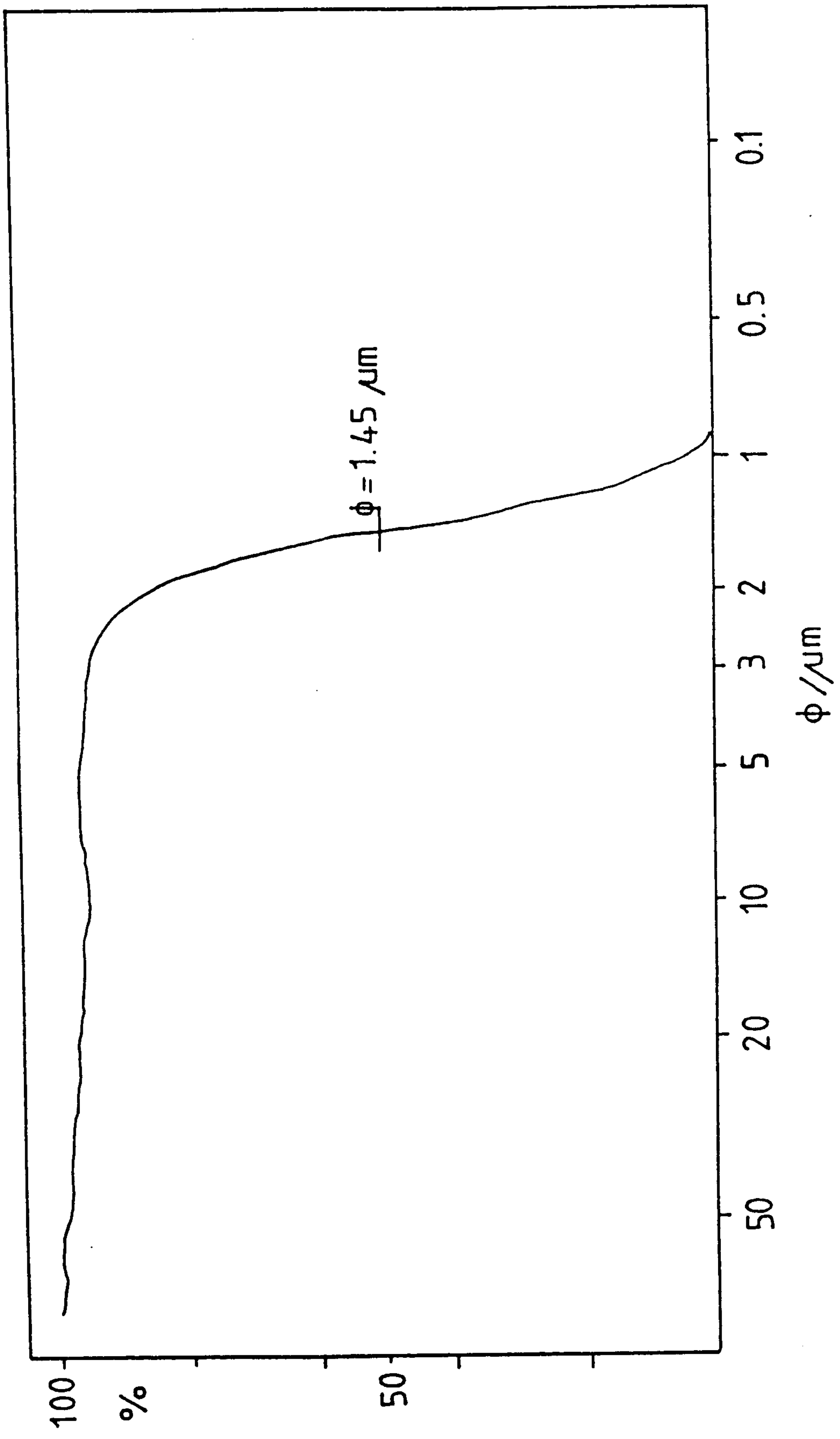

FIG. 3.

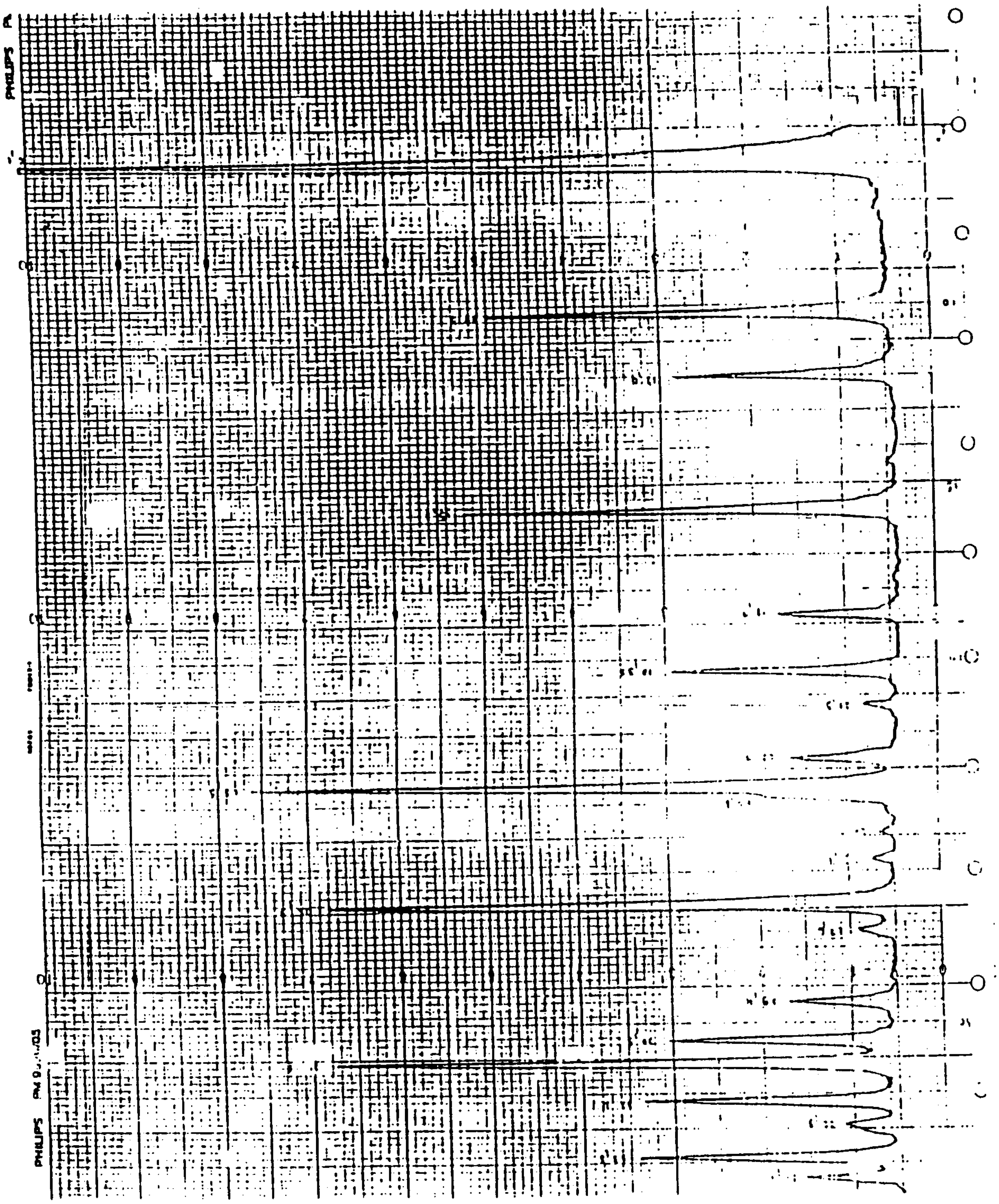

FIG. 4.

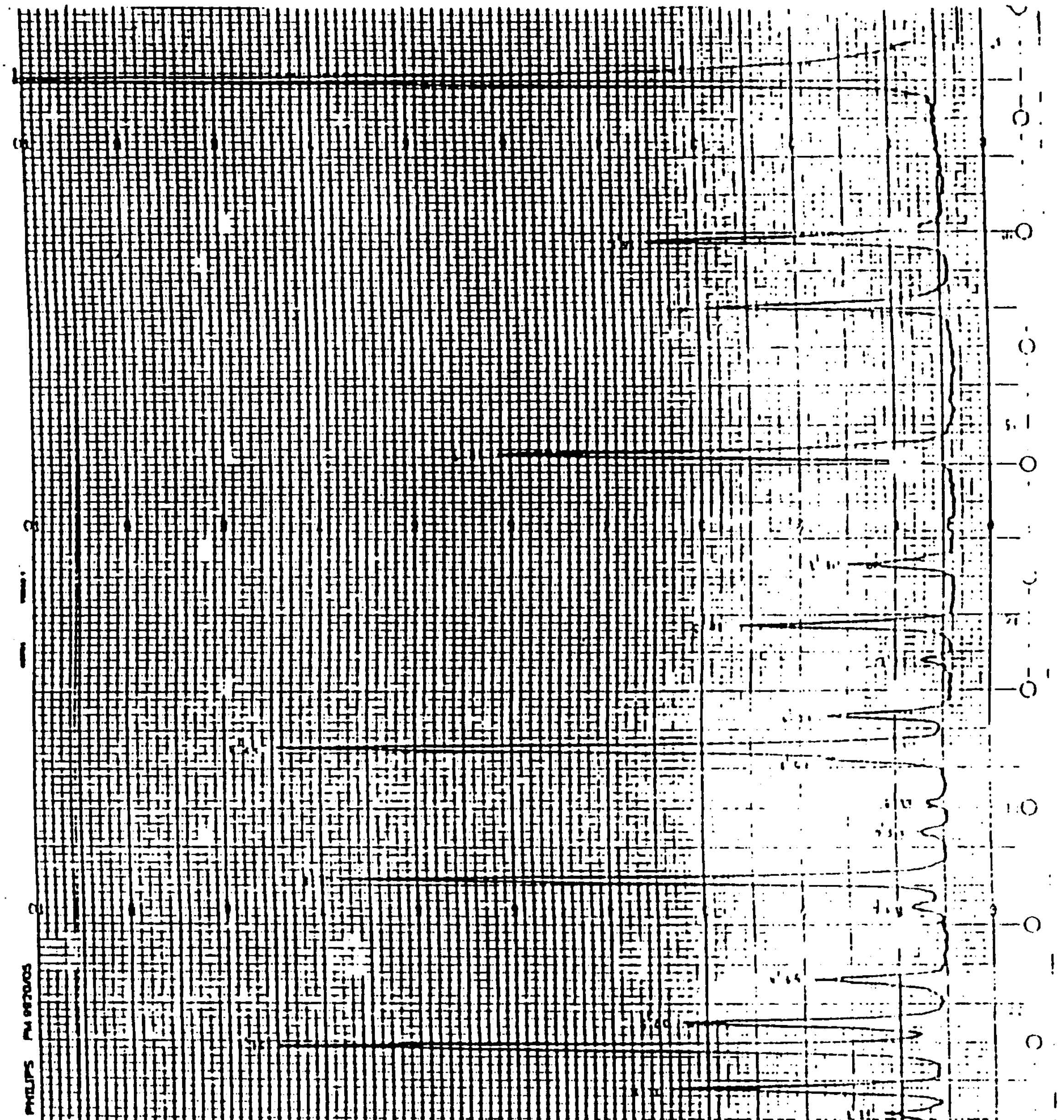

FIG. 5.

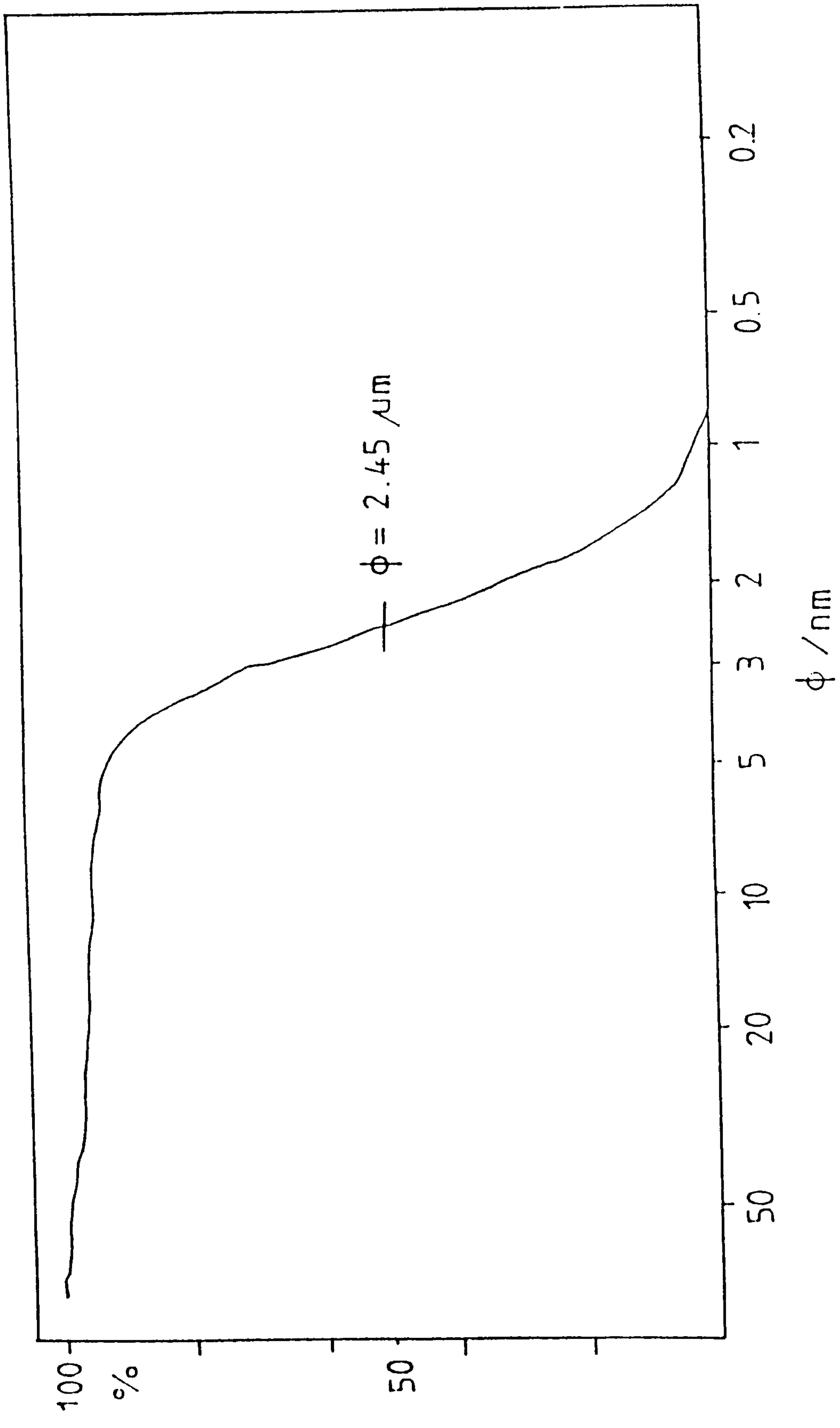

FIG. 6.

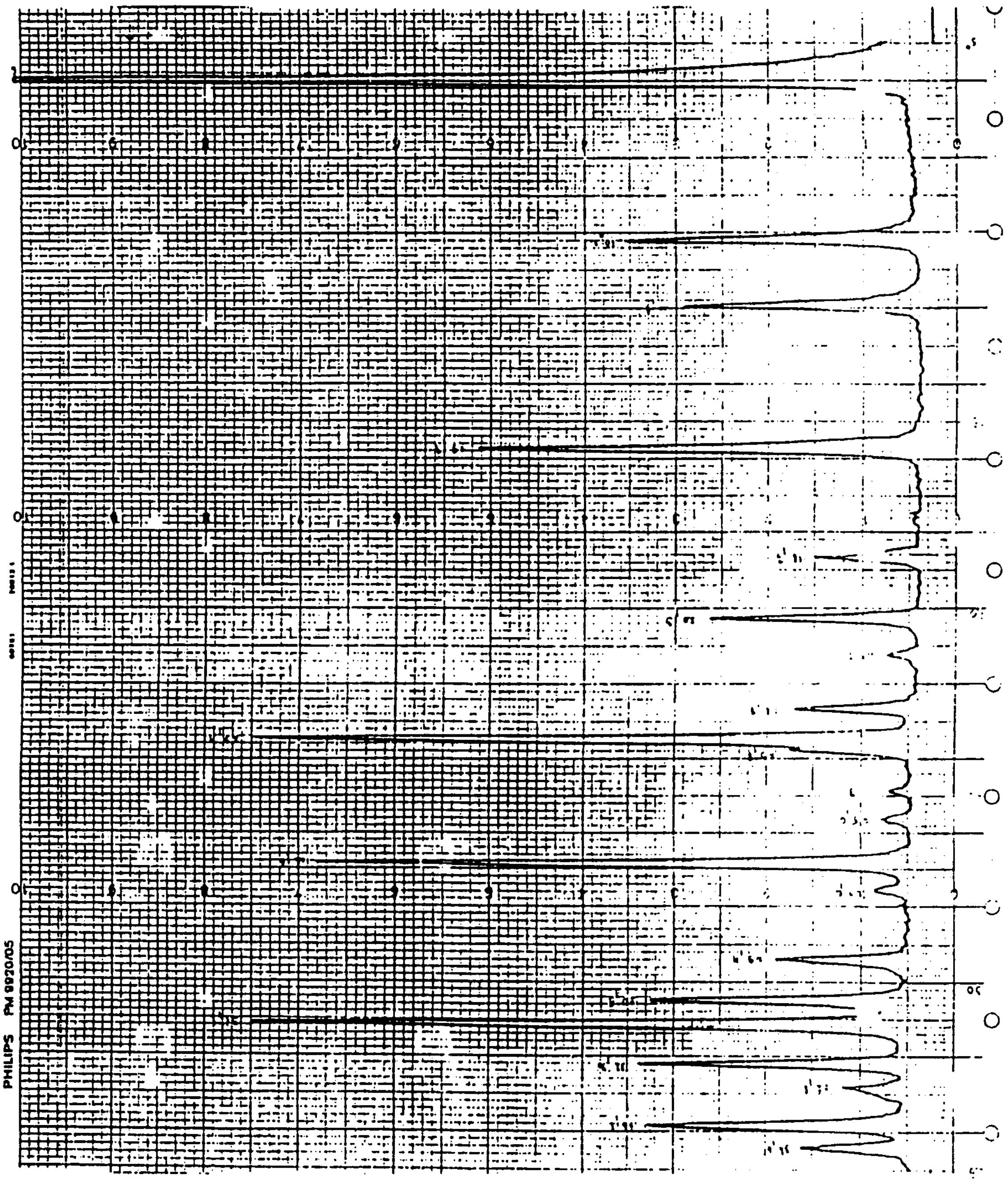

FIG. 7.

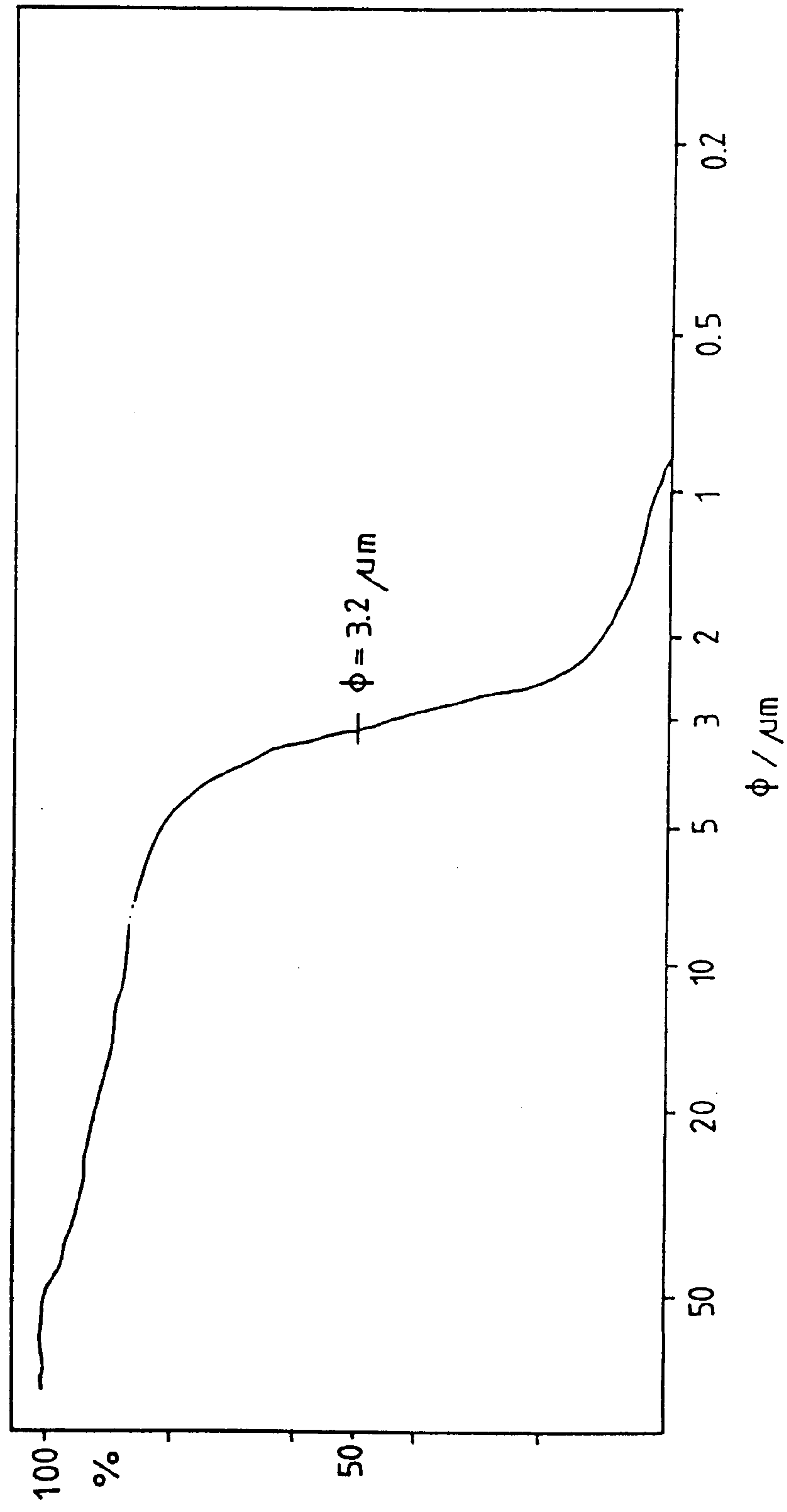

FIG. 8.

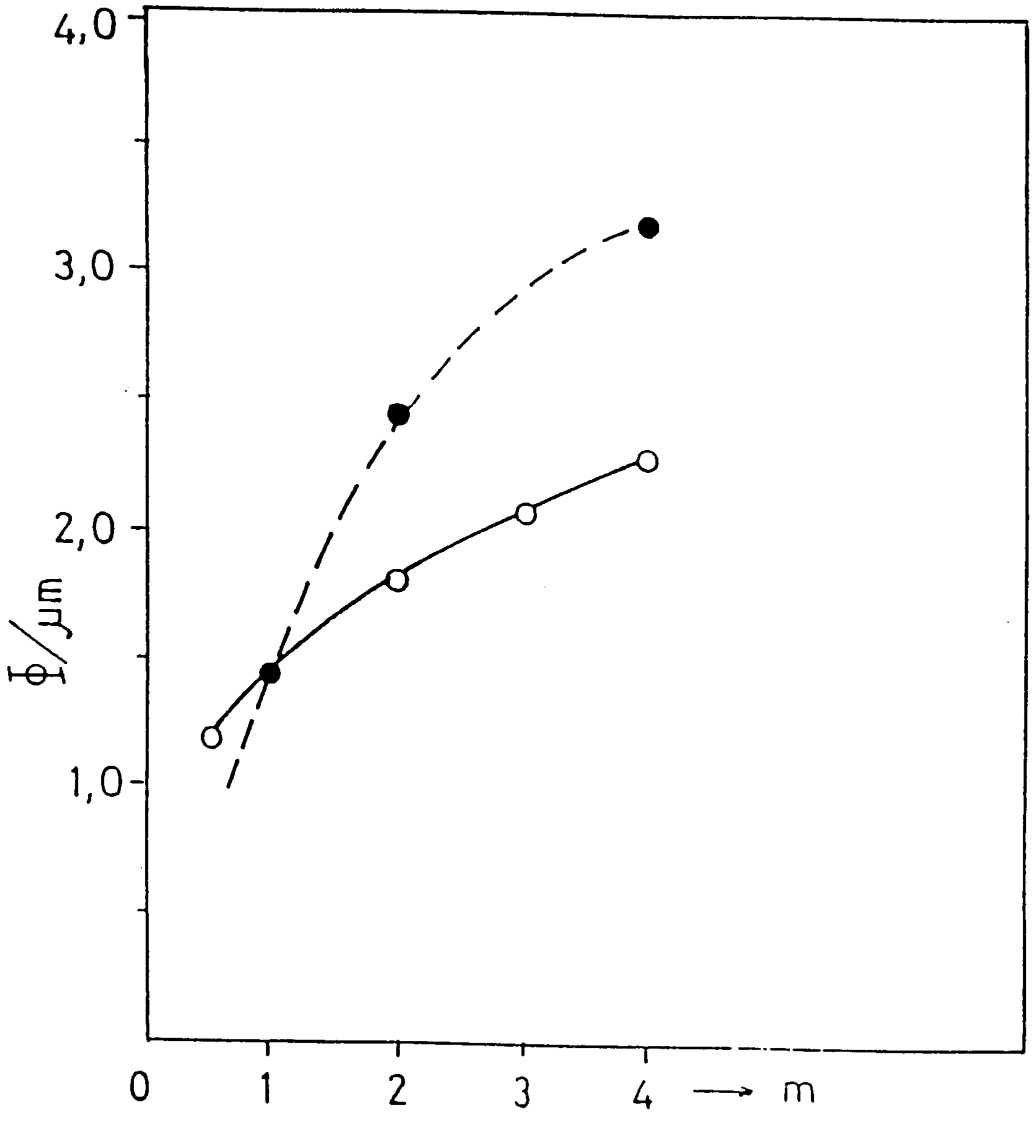

FIG. 9.

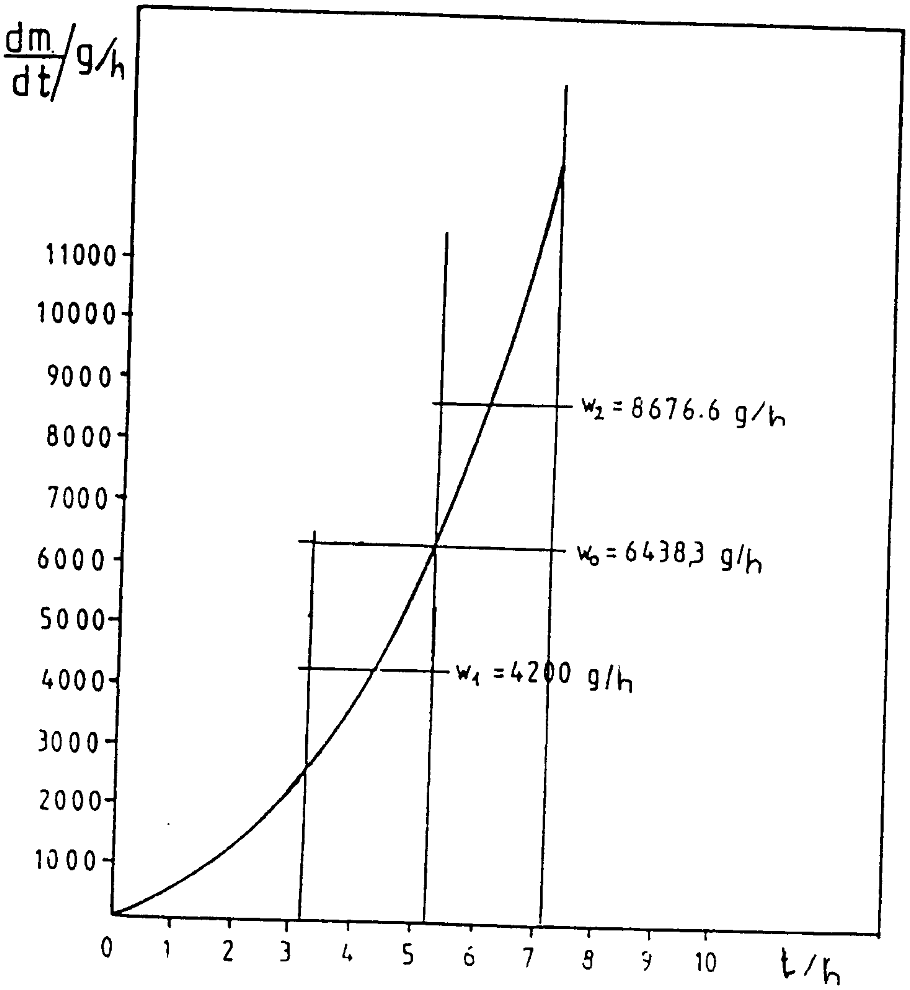
dm/dt / g/h
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1
2
3
4
5
6
7
8
9
10
t/h
w₂ = 8676.6 g/h
w₀ = 6438,3 g/h
w₁ = 4200 g/h

FIG. 10.

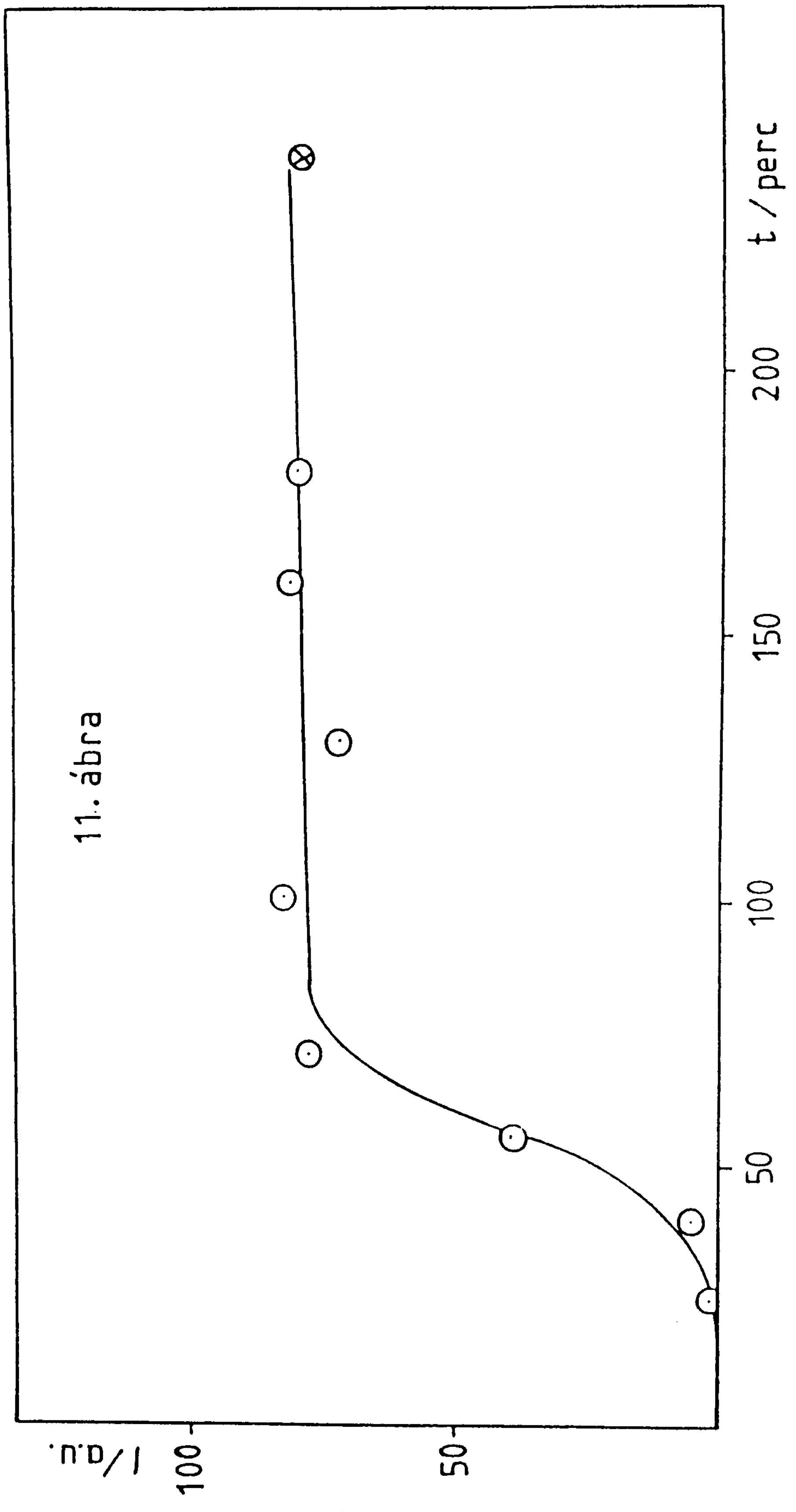

FIG. 11.

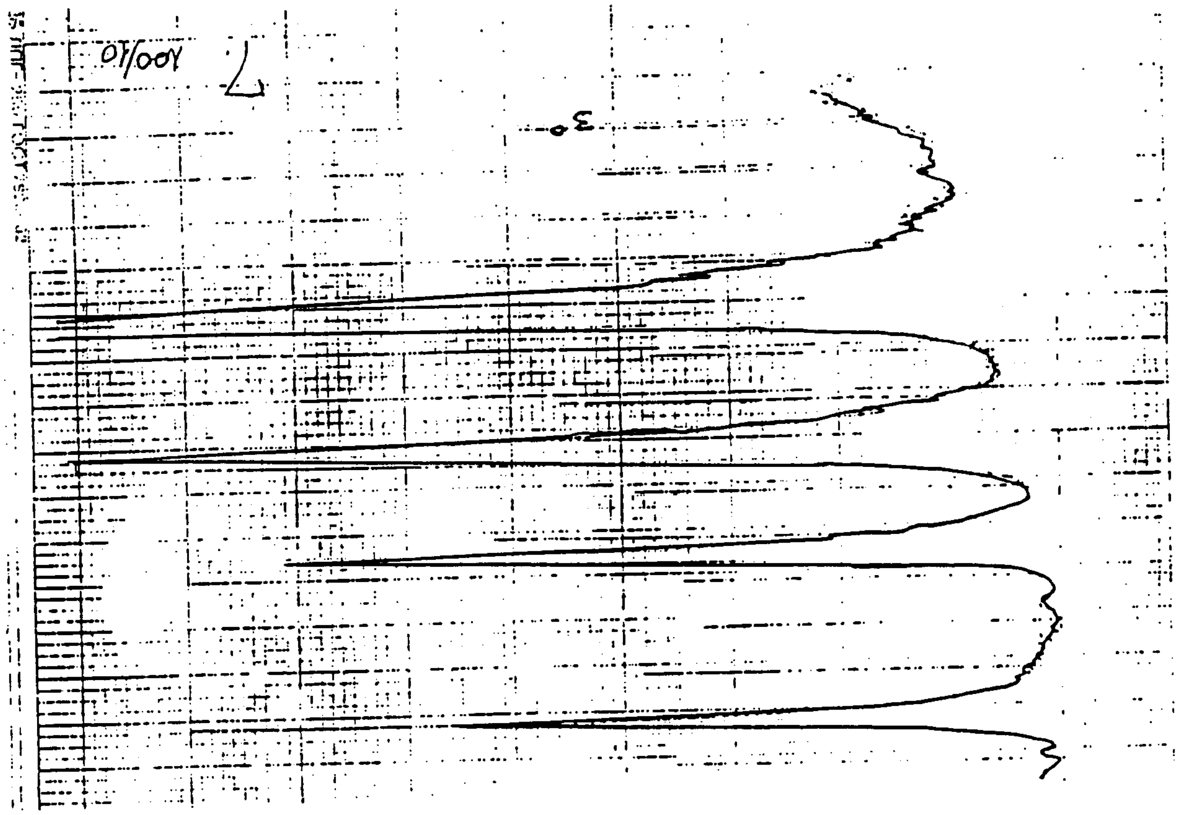

FIG. 12.

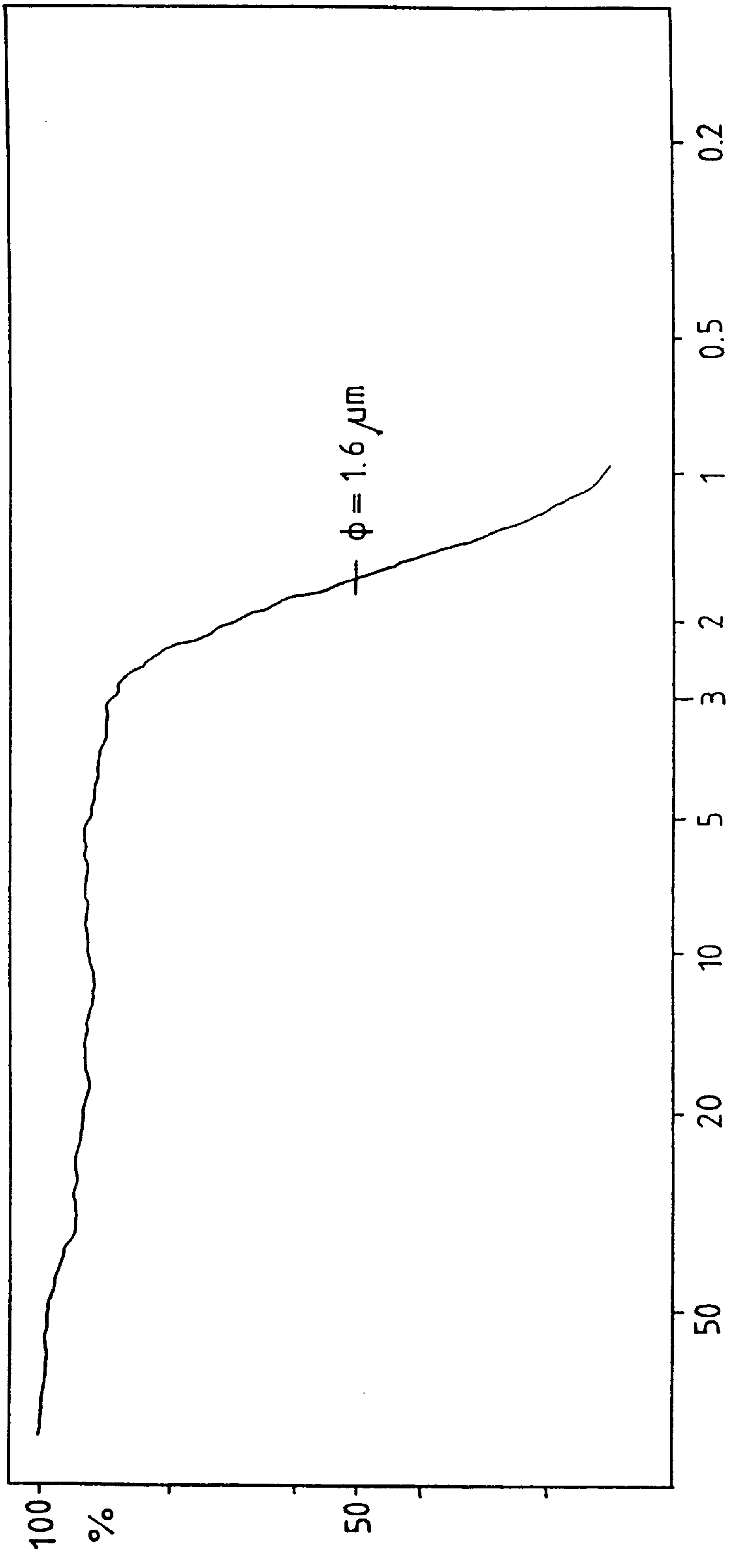

FIG. 13.

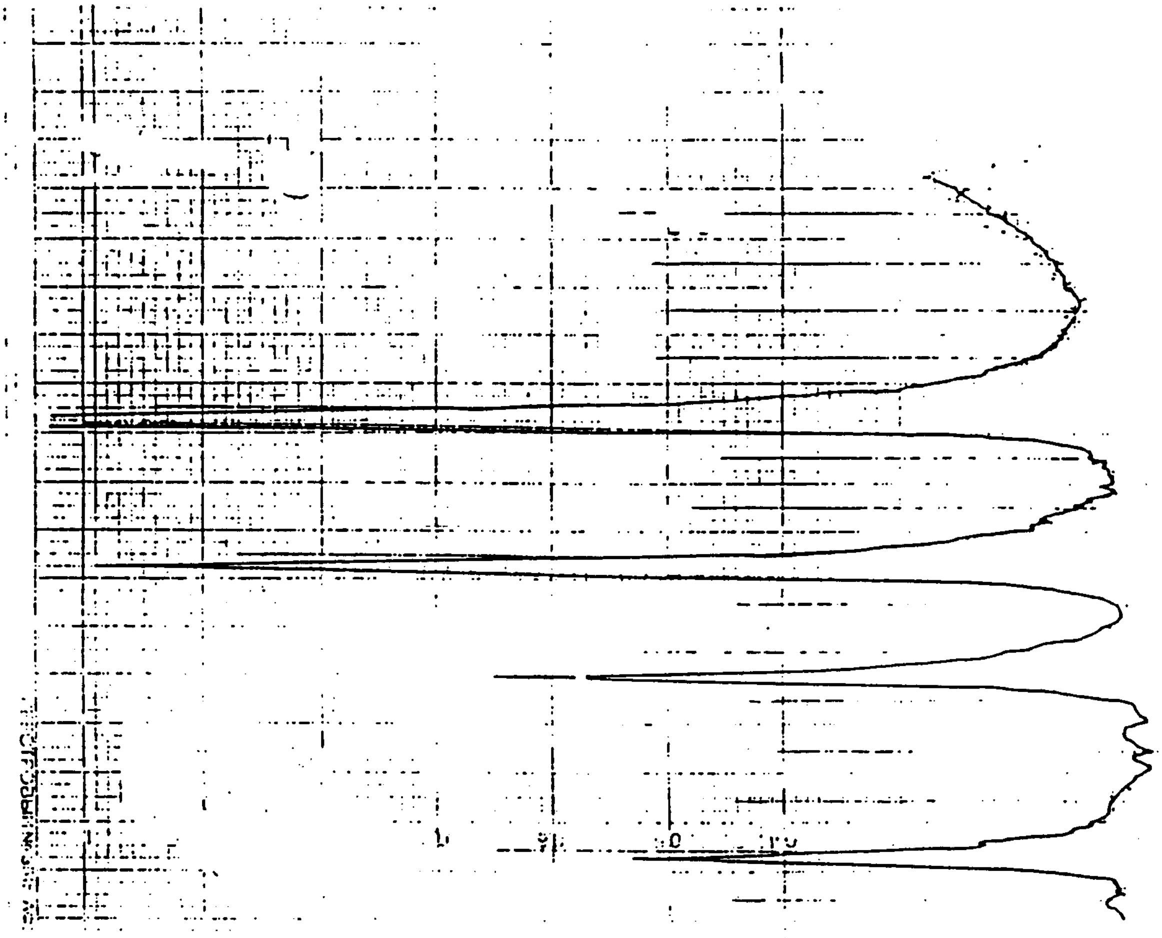

FIG. 14.

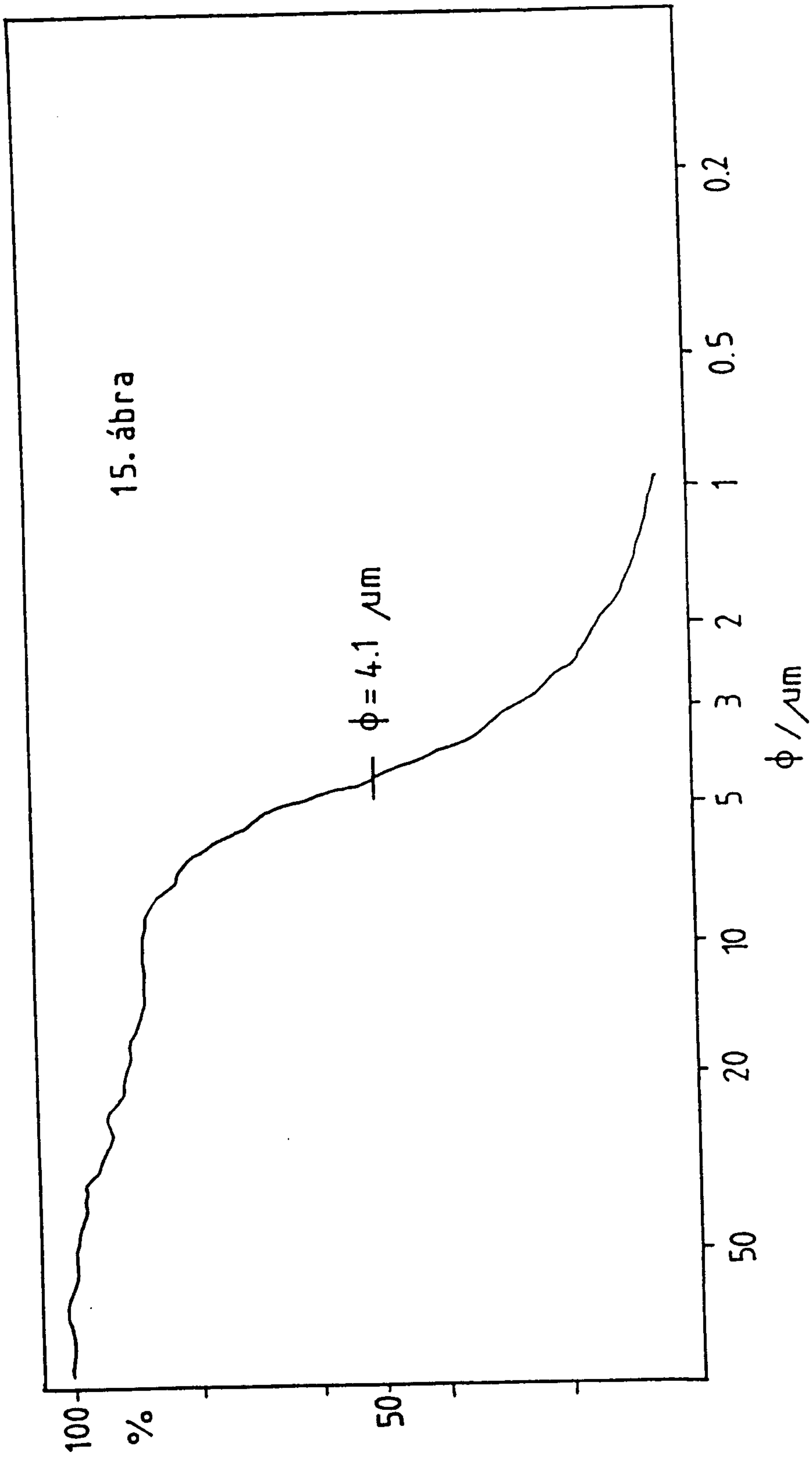

FIG. 15.

INTERNATIONAL SEARCH REPORT

Inter   nal Application No
PCT/HU 99/00073

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C01B39/16

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   C01B

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 340 573 A (VAUGHAN DAVID E W ET AL) 20 July 1982 (1982-07-20) cited in the application example 1	1
A	FR 2 339 571 A (GRACE W R LTD) 26 August 1977 (1977-08-26) claim 1 & US 4 178 352 A cited in the application	1
A	GB 2 043 043 A (TOYO SODA MFG CO LTD) 1 October 1980 (1980-10-01) claim 1	1
A	US 3 510 258 A (HINDIN SAUL G ET AL) 5 May 1970 (1970-05-05) claim 1	1

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 15 March 2000	Date of mailing of the international search report 31/03/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Clement, J-P

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INTERNATIONAL SEARCH REPORT

Inten nal Application No
PCT/HU 99/00073

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	DE 27 44 784 B (BASF AG) 17 August 1978 (1978-08-17) claim 1	1
X	EP 0 034 696 A (DEGUSSA ;HENKEL KGAA (DE)) 2 September 1981 (1981-09-02) page 2, line 33 - line 35	7
A	DE 43 09 656 A (HENKEL KGAA) 29 September 1994 (1994-09-29) claim 1	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/HU 99/00073

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4340573 A	20-07-1982	NONE	
FR 2339571 A	26-08-1977	AU 505874 B	06-12-1979
		AU 2184077 A	10-08-1978
		CA 1082671 A	29-07-1980
		DE 2703264 A	04-08-1977
		GB 1560223 A	30-01-1980
		IT 1091561 B	06-07-1985
		JP 1376322 C	22-04-1987
		JP 52094899 A	09-08-1977
		JP 61037206 B	22-08-1986
		MX 144258 A	18-09-1981
		NL 7700908 A	02-08-1977
		US 4178352 A	11-12-1979
		ZA 7700535 A	28-12-1977
GB 2043043 A	01-10-1980	JP 1231410 C	26-09-1984
		JP 55104914 A	11-08-1980
		JP 59007643 B	20-02-1984
		JP 1231412 C	26-09-1984
		JP 55116618 A	08-09-1980
		JP 59007644 B	20-02-1984
		AU 538193 B	02-08-1984
		AU 5526680 A	14-08-1980
		DE 3004060 A	21-08-1980
		US 4376106 A	08-03-1983
US 3510258 A	05-05-1970	DE 1667475 A	09-06-1971
		GB 1167775 A	22-10-1969
		JP 49013720 B	02-04-1974
DE 2744784 B	17-08-1978	NONE	
EP 0034696 A	02-09-1981	DE 3007080 A	10-09-1981
		AT 7378 T	15-05-1984
		BR 8101035 A	01-09-1981
		CA 1150222 A	19-07-1983
		ES 499768 D	01-12-1981
		ES 8201103 A	01-03-1982
		FI 810442 A,B,	27-08-1981
		JP 1350277 C	28-11-1986
		JP 56134515 A	21-10-1981
		JP 61014081 B	17-04-1986
		US 4339419 A	13-07-1982
DE 4309656 A	29-09-1994	AT 154794 T	15-07-1997
		DE 59403220 D	31-07-1997
		WO 9421558 A	29-09-1994
		EP 0690821 A	10-01-1996
		JP 8508003 T	27-08-1996
		US 5645811 A	08-07-1997