EUROPEAN QUALIFYING EXAMINATION 1995

PAPER A
CHEMISTRY

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95/A(C)/e

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 practise 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.

PAPER A/1995 (Chemistry)

Dear Sir/Madam,

As newcomers to the European patent system we have heard from friends that your firm has experience in prosecuting European patent applications, and so we have decided to entrust you with our first European patent application.

Allow me first to introduce my company: we operate mainly in the field of chemical plant construction and thus also carry out research on materials for use in plant construction.

Our invention is the result of metallurgical investigations in connection with an order for a special chemical production plant. Our client is faced with corrosion problems in his urea plant and would like to see them resolved now that a new plant is to be constructed. He furthermore wishes to ensure that the urea produced is not contaminated by corrosion products.

Numerous solutions have been proposed for reducing corrosion in such plants but these have often been either very costly or very complicated and thus difficult to put into practice, or both.

We started by investigating the chemical reaction as such. We wanted to find out whether the difficulties could be resolved by changing the reaction parameters. It was soon evident, however, that any reduction in corrosion achieved in this way had the undesirable side-effect of reducing yield to a level which was uneconomical. The search for a solution therefore had to be approached differently, i.e. by selecting the right material for building the reactor, with due consideration for the price.

It has been known since the early days of chemical plant construction that lead (**Pb**) is highly resistant to corrosion from many materials. It is sufficient to mention the lead chamber process for the manufacture of sulphuric acid as well as the use of lead pipes for drinking-water supply. However, lead has been eliminated from our considerations because of its inadequate mechanical strength. There is thus no need to go into the other disadvantages of lead, such as its poisonous properties. It is also known that lead alloyed even with small quantities of other metals, such as antimony (**Sb**), tin (**Sn**) and/or arsenic (**As**), assumes markedly different properties.

However, we have now established that certain Pb-Sb alloys are characterised by very high resistance to corrosion from aggressive media. If such alloys are to be used in the construction of chemical plant, this property on its own is not sufficient. These alloys must also meet certain mechanical requirements. We have now found a way of manufacturing Pb-Sb alloys with very good chemical resistance and good mechanical properties. These meet the requirements and the material has the potential for a wide variety of uses in chemical plant construction. If the inside reactor walls, which are in contact with the reaction mixture, are manufactured from this material, because of their greater strength a simpler outer construction can be used for the reactor than was hitherto necessary.

The processing of lead and antimony is not entirely straightforward even in the binary system, despite the apparent simplicity of composition. Whilst molten Pb and Sb can be mixed in almost any proportions, inhomogeneities can occur in the solid state when they cool, as a result of separation. The properties of the Pb-Sb alloy thus greatly depend on the conditions of manufacture. This also applies near the eutectic, which is known to be 11.1% by weight of Sb. A construction material for chemical production plant must of course be homogeneous if it is to

be of good strength, to ensure that within the material there are no variations in its prope[rty] as a result, minimal corrosion, and that it will provide a high degree of safety and have [a] useful life (service life).

In order to achieve this, the alloy must be prepared by a special process which I shall now describe.

For this purpose, Pb and Sb are melted together in suitable quantities. More precisely, the appropriate quantity of lead is usually melted in an induction furnace in inert crucibles and covered with a protective anti-oxidant melt consisting of a salt with a low melting point. The requisite quantity of Sb is added through this protective melt with a strong intermixing action at temperatures normally above 400°C. A proportion of 15% by weight of Sb should on no account be exceeded. The hardness of this material becomes greater, the higher the proportion of Sb in this range. However, at the same time the material becomes more brittle. Above the 15% limit the material is also more likely to contain the inhomogeneities mentioned earlier, which make the product unsuitable for the present purpose. Material with less than 1% by weight of Sb does not have the desired properties.

For casting, the protective melt is skimmed off and the molten alloy can then be cast at 400°C in steel moulds for example. Up to this point, our process is no different to that used hitherto in the manufacture of these or similar lead alloys.

In the traditional method, preheated moulds are used and the alloys are then allowed to cool in them to ambient temperature. The alloys solidify at above approximately 250°C. They are then processed as desired, for example by rolling or recasting. As already pointed out, further processing in this way would not result in a material corresponding to our requirements.

For that reason, the still liquid alloy in the moulds is treated differently in our process. It is quenched with a cooling agent, immediately after casting, to a temperature of less than 200°C, so that no inhomogeneities can occur.

To reach the strength values required for plant construction, the formed bodies (bars) obtained as described above are heated, before further processing, to a temperature of from 135° to 175°C if they have cooled below that level. They are then rolled within this temperature range, for which purpose a lubricant (generally kerosene) is normally used. The thickness of the formed bodies is reduced with each pass by 10 to 20%. The bars or plates rolled in this way are then finish-rolled with their thickness being reduced again by at least 10%, at a rate of 1 to 5% per pass. The rolling temperature in the finish-rolling operation ranges from room temperature (20°C) to 125°C, depending on the exact composition and the exact requirements to be met by the alloy.

Experiments have shown that the alloys for plant construction, especially in the case of urea production plants, should preferably not contain more than 5% by weight of Sb. Above that limit, the number of cracks which can appear in the finish-rolling operation (as a result of the increased brittleness mentioned) rises steeply and weakens the material. It can also be observed that the mechanical strength of the alloy is greater the nearer the finish-rolling temperature is to the upper limit of the stated range. The reduction in thickness after each pass at the finish-rolling stage also influences the mechanical properties. We have discovered too that those of our alloys which have not undergone the special rolling process were comparatively "softer", i.e. they were not as strong, even though their chemical resistance was the same as that of the finish-rolled product.

This presents the possibility of constructing a reactor with inner walls, which can come into contact with the reaction mixture, consisting of plates made of the hardened alloy, and of using

unhardened alloy of the same composition for the joints between the plates. The chief a...
of such a construction is avoidance of contact corrosion. Another advantage is the s...
structure from the point of view of expansion and contraction as temperatures change: The so...
material in the joints between the plates is more ductile and can prevent leakages. When the join...
is being cast, steps must be taken, if appropriate by means of additional cooling, to ensure that
heat is quickly dissipated so as to avoid inhomogeneities in the joint filling such as those steps
already mentioned in connection with the mould casting.

We have also investigated in detail the interaction between the alloy and the urea, and especially
the absorption of alloy constituents by the urea. This was necessary because our customer wishes
to convert some of the urea which he manufactures into biuret for use as an additive in animal
feed. It is thus desirable that additional purification of the organic product should not be
necessary. No traces of the alloy constituents could be found in the urea even when it was left
in the reactor for long periods in reaction conditions going well beyond the usual period of
contact.

One point which has not yet been discussed is the purity of the metals used in the alloy. The
metals would generally be of standard quality, but they should preferably not contain a total of
more than 0.05% by weight of impurities as otherwise their properties could be subject to
unforeseeable changes which would often make them unsuitable for our purposes. Apart from
such impurities, our alloys comprise the constituents indicated, which together must add up
to 100%.

Whilst binary alloys produce the desired results in chemical reactors, the presence of a third alloy
metal where the ternary alloy is to be used as a corrosion-resistant slide bearing metal, for
example as an axle-bearing metal for moderate loads and speeds, might be desired. We found
suitable compositions for this purpose to be 84 to 89% by weight of Pb, 6 to 12% by weight of
Sb and 2 to 8% by weight of Sn. The alloy metals were melted together as described above. The
formed bodies are prepared from these alloys by casting and were hardened by quenching them
to the solid state immediately after casting in the way described above, and cooled further
directly by means of the cooling agent. We consider that this ancillary aspect should also be
included in, and covered by the application.

To enable you to draft the patent application in the best possible way, the results of our
experiments are set out in the following tables and some background literature is enclosed. In the
experiments all the percentages relate to the total weight of the alloy.

The alloys were in all cases manufactured by melting the alloy components together as described
above, and the resulting formed bodies were manufactured by casting in moulds and quenching
to below 200°C.

Table 1

Influence of Sb content and the temperature at which finish-rolling was carried out w reduction in thickness after each of 12 passes

Temperature (°C)	Sb (% by weight)	Tensile strength (MPa)
20	1.0	20.3
20	2.0	22.4
20	5.0	25.2
20	10.0	25.2
125	1.0	23.1
125	2.0	28.0
125	5.0	34.6
125	10.0	34.7
130	2.0	19.5
160	2.0	18.7
160	5.0	18.5
200	2.0	17.8
225	10.0	13.7

The results show that the tensile strength increases with the Sb content but that as soon as the Sb content reaches 5%, added Sb has scarcely any further influence and some small cracks appear. Finish-rolling at a higher temperature with a fixed Sb content results in higher tensile strength, but above 125°C the effect is reversed and tensile strength falls below the minimum value acceptable for plant construction, namely 20 MPa.

Table 2

Influence of reduced thickness per pass in the finish-rolling process with an Sb content of 5% by weight

Temperature (°C)	Thickness reduction (%)	Tensile strength (MPa)	Surface
125	1	34.6	(a)
125	3	34.4	(a)
125	5	33.8	(b)

(a) completely smooth   (b) hair cracks in places

Urea was manufactured in accordance with the usual well-known continuous process from NH_3 and CO_2 via the ammonium carbamate intermediate stage. During the process, pressure of 10 to 30 MPa built up in the reactor at 160 to 200°C.

In an experimental reactor 1, three experimental plates were used as substitutes for existing plates. All the plates were the same size. Plate 1 was of the standard type used in state-of-the-art plant and was made of pure nickel (Ni), plate 2 was made of a lead-bismuth (Pb-Bi) alloy with 2.5% of Bi and plate 3 consisted of a Pb-Sb alloy with 2.5% of Sb which had, in accordance with our invention, been quenched, rolled twice at 175°C (with 15% thickness reduction at each pass) and finish-rolled six times at 110°C with 2% thickness reduction per

pass. After two months of continuous operation, the reactor was switched off ~~and the~~ experimental plates were removed. The plates were given a visual inspection and the cor~~rosion~~ depth was measured (see table 3).

Table 3

Plate 1 entire surface attacked, average depth 3 mm
2 partially attacked (approx. 25% of surface), average depth 1.5 mm
3 a few small marks (approx. 1 mm in diameter), 0.1 mm deep.

The positive effect of the Pb-Sb alloy is clearly demonstrated. However, the slight traces of corrosion on plate 3 were not evenly distributed, but were concentrated on the areas of the plate which had been in contact with other materials. Some Ni and traces of Pb and Bi were found in the urea.

In an experimental reactor 2 of the same type, in which all the plates were of the above plate 3 type, the plate joints were also cast with an alloy of the same composition as the plates. The plates dissipate so much of the heat that this quenching prevents inhomogeneities from being formed in the joints. In the urea produced in this reactor, there were found no traces of either lead or antimony. The plates showed even less corrosion than in the reactor 1 described above.

In order to verify resistance to corrosion, test strips from plates of the composition given in table 4 were immersed in fuming sulphuric acid at 45°C for six weeks. The test strips were then removed, rinsed carefully and dried. Resistance to corrosion was measured on the basis of weight loss. A Pb-Bi alloy with 3% Bi (the material normally used in the lead chamber process) was used for comparison.

Table 4

Each Pb-Sb plate was triple-rolled at 150°C with 10% thickness reduction after each pass, finish-rolled at 125°C and with 1% thickness reduction after each of 12 passes.

Pb-Bi		10,0% loss
Pb -	0.1% Sb	8.0%
	0.5%	6.0%
	1.0%	0.2%
	1.5%	0.09%
	2.5%	0.06%
	3.0%	0.08%
	5.0%	0.1%
	6.0%	4.0%

Although the alloy with 6% Sb is still highly corrosion-resistant, the material is already mechanically less suitable for heavy-duty industrial use: the corrosion advances along cracks in the material. No such cracks were observed in alloys with a lower Sb content.

DOCUMENT I (State of the Art)

Water pipes have for a long time been made from lead. Manufacturing such pipes is a simple and reliable process. The pipes can be easily adapted to fit the requirements of the building site due to their good bending qualities and are well-suited for soldering, which is also an advantage later in the event of repairs. Furthermore, one of the reasons for using lead pipes for water supply is that a coating of low solubility forms on the surfaces which protects the pipe against corrosion.

However, the known pipes have a number of serious disadvantages. Lead is very soft, and the mechanical strength of the pipes is therefore inadequate over the long term. This disadvantage is particularly serious at threaded connections subject to mechanical loads. The coating is repeatedly damaged at points where the lead pipe is subject to mechanical loads. Drinking water often contains foreign ions which attack the coating of the lead pipes.

The use of pure lead pipes in water pipe construction is thus no longer tolerable in the long term.

In contrast to this situation, we have now found that various lead alloys have greatly improved properties and are not only suitable for water pipe construction but, because of their improved hardness, tensile strength and resistance to corrosion are also suitable for other uses. To cite just a few examples, they can be used for printers' type, bearing metal, roofing or as a repair material for other metallic materials. The alloys according to the invention are very suitable for soldering and can themselves be used as soldering material.

The subject-matter of the invention is lead alloys having a lead content of at least 80% by weight and with at least one alloy metal selected from the group bismuth, antimony and tin in quantities of 1 to 15% by weight in each case. Other elements, such as poisonous arsenic, should be kept below 0.3% by weight.

Good examples of our alloys are (percentages by weight):
Pb 95/Bi 5; Pb 89/Sb 11; Pb 97.5/Sb 2.5; Pb 97.5/Bi 2.5; Pb 97.5/Sn 2.5; Pb 89/Sb 7/Sn 4; Pb 86/Sb 9/Sn 5.

The alloys can be obtained by simply melting the metals together, by dissolving the added metals in molten lead or by mixing the molten metals at a temperature of about 400°C. To prevent oxidation it has often proved advantageous to cover the surface of the molten metals with a protective melt of salts having a low melting point, which can be easily removed before solidification. The molten alloys are cast in moulds and left to solidify. They can then be processed further in the traditional manner to form pipes or plates.

DOCUMENT II (State of the Art)

The use of acids requires materials resistant to these products. Experiments have shown that lead antimony alloys in a suitable composition manufactured by a special method, give satisfactory results. This new alloy can replace the traditional lead or enamel lining. Manufacture is quite simple: lead is melted in a hermetically sealed furnace; antimony is melted nearby in another container. When the antimony has turned dark red, it is poured into the lead and thoroughly stirred and the alloy is then allowed to cool.

The table gives the pressure which the alloy is able to withstand at a given wall thickness (% = % by weight)

Pressure in MPa	% Sb	Thickness in cm
0.15	1.0	3.0
0.2	2.0	3.0
0.2	3.0	2.0
0.3	4.0	2.0
0.5	5.0	2.5
0.6	6.0	3.0
0.8	7.0	3.5
1.0	8.0	4.0