

February 11, 1938

Mr. J. H. Schaefer
Ethyl Gasoline Corporation
P. O. Box 688
Wilmington, Delaware

Dear Mr. Schaefer:

The item marked "Overhead" and charged to the tetraethyl lead operation, as queried by your letter of February 7th, is a proper and direct charge against the manufacturing operations. For some time past the DuPont Company has paid for services rendered in the maintenance of proper control of the manufacturing operations. This charge includes the cost of medical supervision at the Dye Works Plant and at Baton Rouge, and also the cost of analytical services in checking the excreta of representative employees. This sum has previously been paid direct to me, to be administered by me personally. However, with the beginning of this year, I suggested the impropriety of this arrangement and requested that the sum be paid to the University in quarterly installments. The sum made available in this way was based on the cost of the previous year's work with the understanding that at quarterly intervals an accounting would be rendered to DuPont so that they would not pay more or less than the actual cost of the services. In as much as most of this service is rendered by the laboratory proper, it seemed only fitting that it should be paid into the University through the usual channels. For your own private information, I might point out that DuPont is not making any contribution toward the experimental work of the laboratory except to the extent that these analytical data are useful to us in our study of the general problem.

Very truly yours,

RAK:is

Robert A. Kehoe, M.D.

KE 0000939

ETHYL GASOLINE CORPORATION

MANUFACTURING AND TRAFFIC DEPARTMENT

INTER-OFFICE
CORRESPONDENCE

MAIL ADDRESS: BOX 1271, WILMINGTON, DEL.
FREIGHT ADDRESS: CARNEY'S POINT, N.J.
TELEPHONE: PENNS GROVE, N.J. 280, EXTENSION 213.

February 7, 1938

(Personal and Confidential)

Dr. Robert A. Kehoe

Dear Bob:

About six months ago you asked me to develop through I.G. further information on the patent application for introducing certain alkali metal fluorides for stabilizing tetraethyl lead and anti-knock mixtures containing same, particularly by the method of heating and refluxing ETHYL Fluid or tetraethyl lead with the stabilizer.

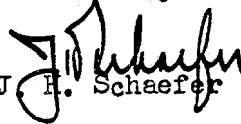
Attached is reply dated February 1, from Chemnyco Inc., New York. Apparently, a long time was required for their reply.

You will note another application was presented to the U.S. Patent office for the solution of the alkali metal fluorides in tetraethyl lead, or ETHYL Fluid, by a common solvent, monohydric alcohols, and more specifically, methanol.

Both applications are under final rejection and probably nothing of importance will be obtained.

The first named application above carries statutory expiration period of February 13, and the second, March 1. Please wire me at once if you have any further interest.

Yours truly


J. H. Schaefer

A:AB

KE 0000940

CHEMNYCO INC.

521 Fifth Avenue

New York

February 1, 1938.

Ethyl Gasoline Corporation
Manufacturing and Traffic Department
Box 1271
Wilmington, Del.

Attention of Mr. J. H. Schaefer

Gentlemen:

About half a year ago, you asked us for information from the I.G. Farbenindustrie Aktiengesellschaft on the use of certain alkali metal fluorides for stabilizing lead tetraethyl and anti-knock mixtures containing the same.

We are now informed by our patent attorneys, Messrs. Hutz & Joslin, that the U.S. Patent Applications Serial Nos. 101 079 and 101 080 covering this invention are under final rejection. Although we are not certain as to whether I.G. Farbenindustrie consider the two applications as coming under their license agreement with the Ethyl G.m.b.H., we would like to draw your attention to this matter. Attached we send you a photostat copy each of the applications serial nos. 101 079 and 101 080, together with one photostat copy each of the Office Actions and amendments which have been filed in these cases. Messrs. Hutz & Joslin comment on the situation as follows:

"Both cases are under final rejection and we are reasonably certain that nothing of importance can be obtained in them by interviewing the Assistant or Primary Examiners and are very doubtful whether an appeal would be successful. The statutory period expires in 101,080 on February 13 and in 101,079 on March 1, 1938."

Please let us know whether the Ethyl Gasoline Corporation has any further interest in the applications. In view of the statutory period expiring very soon, an early reply would be appreciated.

Very truly yours,

CHEMNYCO INC.

C. Mueller

Encls.
Dr. CM:S

KE 0000941

This invention relates to a process of stabilizing lead tetraethyl and anti-knock mixtures containing the same.

The "anti-knock" agents which have of late been extensively used as additions to motor fuels and which contain, as active constituent, lead tetraethyl in admixture with other organic compounds, have the undesirable property of gradually decomposing during storage, particularly when exposed to light.

It has already been proposed to counteract this tendency of lead tetraethyl to decompose, by adding to the anti-knock agents, or the motor fuels containing the same, water-soluble fluorides, and more particularly neutral alkali metal fluorides, in extremely minute doses (a few parts in ten thousand). These extremely minute additions generally suffice to prevent decomposition of the lead tetraethyl, when the latter has already been added to the motor fuel, since the amount of alkali metal fluoride needed to stabilise the lead tetraethyl is readily absorbed by motor fuels owing to its being soluble therein to an appreciable extent. However, in the case of lead tetraethyl alone, or in the case of the usual mixtures of that substance with other organic substances serving to lower the vapour pressure, absorption does not take place to the requisite extent, because the alkali fluorides are practically insoluble in lead tetraethyl. In fact, when the amounts of alkali metal fluoride, considered, in accordance with the former proposal, as sufficient, are added to the anti-knock agent itself, decomposition phenomena, due to insufficient solubility of the added stabilizer, will nevertheless make their appearance, during storage under exposure to light, and ultimately result in the mixture becoming thoroughly spoiled.

It has now been ascertained in accordance with the present invention that lead tetraethyl can be caused to absorb the amount of alkali metal fluoride required for its stabilisation, by adding the alkali metal fluoride to the lead tetraethyl in presence of substances having a solvent action both on the fluoride and on the lead

The monohydric alcohols have been found particularly suitable for this purpose.

In this manner, anti-knock agents can be produced which besides containing the lead tetraethyl in the usual concentration contain also sufficient quantities of the alkali metal fluoride not only for stabilising the anti-knock agent when added to a motor fuel, but also for ensuring the stability of the anti-knock agent by itself, even during prolonged storage under exposure to light.

For example, mixtures can be prepared in which the ratio of alkali metal fluoride in solution, to lead tetraethyl exceeds ten times the ratio attainable when the alkali metal fluoride alone is dissolved in the lead tetraethyl.

EXAMPLE.

A 1% solution of potassium fluoride in methanol is prepared, and is mixed, in the proportion of 6:1 with the anti-knock agent, containing lead tetraethyl, known in commerce as "Ethylfluid". The solution of the "Ethylfluid" in the alcoholic potassium fluoride remains perfectly limpid and free from signs of decomposition, even during storage under exposure to light.

I claim:

1) A process for the production of an anti-knock agent containing lead tetraethyl in stable form which comprises dissolving an alkali metal fluoride in the lead tetraethyl in the presence of a substance having a solvent action both on lead tetraethyl and on said alkali metal fluoride.

2) A process for the production of an anti-knock agent containing lead tetraethyl in stable form which comprises dissolving an alkali metal fluoride in the lead tetraethyl in the presence of a monohydric alcohol.

3) A process for the production of an anti-knock agent containing lead tetraethyl in stable form which comprises dissolving an alkali metal fluoride in the lead tetraethyl in the presence of methanol.

4) A composition of matter containing lead tetraethyl in stable form and further an alkali metal fluoride and a substance having a solvent action both on lead tetraethyl and on said alkali metal fluoride.

5) A composition of matter containing lead tetraethyl in stable form and further an alkali metal fluoride and a monohydric alcohol.

6) A composition of matter containing lead tetraethyl in stable form and further an alkali metal fluoride and methanol.

Department of Commerce
United States Patent Office
Washington

Applicant: Josef M. Michel

Ser. No. 101,079
Filed Sept. 16, 1936
For Process for stabilizing
lead tetraethyl and anti-
knock mixtures containing
same

Hutz & Joslin,
621 Fifth Ave.,
New York, N. Y.

References cited:

I. G. Farb. (Br.) (2 sheets)	414,581	Aug. 9, 1931	44-9.01
Midgely	1,592,954	July 20, 1926	44-9.01
Johns	1,757,838	May 6, 1930	44-9.01

It is known that the alkali fluorides enhance the stability of lead ethyl as shown by I. G. Farbenindustrie.

It is common to use a small quantity of alcohol to solubilize the halogen compounds usually used with lead ethyl in gasoline as shown by Midgely; also alcohol is considered to enhance the effectiveness of the lead ethyl as pointed out by Johns. Accordingly lead ethyl in common use may contain a small amount of alcohol, so that the lead ethyl composition of I. G. Farb. may be read as containing some alcohol together with the stabilizing alkali fluoride in view of these references in direct anticipation of the claims.

Claims 1-6 are rejected as unpatentable over I. G. Farb. taken with Midgely or Johns, ex parte Walker 1923 C. D. 39.

Examiner

KE 0000945

N 5669 04

IN THE UNITED STATES PATENT OFFICE

Josef M. Michel

Ser. No. 161 079

Filed Sept. 16, 1936

For PROCESS FOR STABILIZING
LEAD TETRAETHYL AND ANTI-
KNOCK MIXTURES CONTAINING
SAME

Division 64

Room 4708

New York, N.Y., May 27, 1937.

Hon. Commissioner of Patents.

Sir:-

In response to the Office Letter dated 4th December 1936, the Examiner is requested to reconsider his rejection of the claims in this case for the following reasons.

It is admitted that British Patent Specification No. 414 581 generally shows that the presence of alkali fluorides enhances the stability of lead ethyl. The only method of incorporating such fluorides in lead ethyl disclosed in that publication, however, is a mere addition of very small proportions of such fluorides, such proportions being of the order of a few hundredths of one percent. It is noted that lines 75-79 on page 1 of that patent only suggest a method for incorporating the protective fluoride in the fuel containing lead ethyl, but not in the lead ethyl itself.

The Midgely patent U.S. 1 592 954 discloses mixtures of tetra ethyl, tetra phenyl, tetra methyl, tetra amyl, or other similar compound of lead, with various chlorine compounds adapted to supply chlorine which combines with the lead during the combustion to form a lead-chloride compound (compare l.c. page 1, lines 23-32). The patent goes on to state that the corresponding iodide and bromide compounds may be employed in the place of the chloride compounds; but it remains silent with respect to the last and only halogen compounds, viz. the fluorides, which are essential in the

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present combination, and it may be taken that if a similar effect could be obtained with the aid of fluoride compounds then the earlier inventor would not have failed to state this. The Midgely patent, on its face, therefore is an implied statement contrary to the supposition basic to the Examiner's argument, that all halogen compounds with respect to the Midgely patent must be considered equivalents.

Moreover, the Midgely patent on page 1, lines 84-92, states that alkyl dihalide compounds of lead and the trialkyl monohalide compounds of lead are generally less soluble in the usual motor fuels than the tetra alkyl compounds, and suggests that alcohols may be employed to assist in blending these anti-knock compounds with the fuel; this according to applicant's view can only be taken as meaning that there is no reason whatever to employ alcohols in conjunction with tetra alkyl compounds, and the Examiner's statement that "lead ethyl in common use may contain a small amount of alcohol", is thus not supported by the Midgely patent.

It is believed that the foregoing arguments effectively dispose of the Midgely patent as a reference to be used in the rejection of the present claims.

As to the Johns patent U.S. No. 1 757 838, it is noted that the suggestion there is to economise the use of tetra ethyl lead in the doping of motor fuels by adding a smaller amount than usual of tetra ethyl to the fuel, and coincidentally modify the petroleum hydrocarbons (i.e. the fuel) by the addition of a small proportion of an alcohol.

The latter feature thus is inseparably tied up with the treatment of the fuel, and the Examiner's assumption that lead ethyl as such would contain a certain proportion of alcohol is thus not supported by the Johns patent.

Considering that for the foregoing reasons both the Midgely and the Johns patents cannot be made to read on the claims in this case, it is believed that the rejection of the claims as unpatentable over I. G. Farbenindustrie taken with either Midgely or Johns is untenable.

In view of the undisputed fact that the solubility of alkali metal fluorides in tetra ethyl lead is substantially increased by the presence of an alcohol

KE 0000947

over the solubility attainable by a mere addition of fluorides to tetra ethyl lead in the absence of alcohols, and that only the latter procedure is shown in British Patent Specification No. 414,581, it is submitted that the claims in this case are patentable and should therefore be allowed. Such action is respectfully solicited.

Respectfully submitted,

Attorneys for Applicant.

DEPARTMENT OF COMMERCE
United States Patent Office
Washington

Applicant: J. M. Michel

Ser. No. 101,079
Filed Sept. 16, 1936
For PROCESS FOR STABILISING
LEAD TETRAETHYL AND
ANTI-KNOCK MIXTURES
CONTAINING SAME

Hutz & Joslin
521 Fifth Ave.
New York, N. Y.

Responsive to argument filed May 28, 1937.

Applicant's argument is noted. As to British 414,581 applicant contends that insufficient alkali fluorides are used. The difference is that less lead ethyl may have been stabilized than herein, hence more alkali fluoride must be added to stabilize the increased quantity of lead ethyl. The difference, of course, is merely one of degree.

However, the proposal herein is to add a common solvent to increase the solublized quantity of alkali fluorides. The commonest solvent generally used for water soluble compounds in hydrocarbonaceous liquids, even such as lead tetra ethyl would obviously be alcohol. Literally dozens of patents could be cited showing conventional use of alcohol as a common solvent to introduce various dopes into gasolines. It does not appear that in the present instance the selection of alcohol is very effective since anhydrous alcohols are not solvents for alkali fluorides. Hence no particular solvent advantage is found in the use of alcohol herein. When the alleged invention therefore is considered in light of the other references of record, for example, Midgely who proposes to use alcohol to increase the solubility of lead alkyls in gasoline particularly those whose solubility has been impaired by the presences of halogen, no invention is found. So also does no invention appear over Johns who teaches that lead ethyl and alcohol desirably are used in combination in a fuel. Applicant can urge to Johns only the further addition of alkali fluorides to stabilize his lead

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alkyls, but this is already taught by British 414,581. Applicant may urge to British 414,581 the desirable further addition of alcohol, but this is already taught by Johns. The normal practices of what the art already teaches, suggests applicant's combination; hence no invention is present. Ex parte Walker, 1923, C. D. 39.

Since a clear issue is reached, the claims are again and FINALLY rejected upon the references as applied of record.

Examiner

This invention relates to a process of stabilising lead tetraethyl and anti-knock mixtures containing the same.

The "anti-knock" agents which have of late been extensively used as additions to motor fuels and which contain, as active constituent, lead tetra ethyl in admixture with other organic compounds, have the undesirable property of gradually decomposing during storage, particularly when exposed to light.

It has already been proposed to counteract this tendency of lead tetraethyl to decompose, by adding to the anti-knock agents, or the motor fuels containing the same, water-soluble fluorides, in extremely minute doses (a few parts in ten thousand). These extremely minute additions generally suffice to prevent decomposition of the lead tetraethyl, when the latter has already been added to the motor fuel, since the amount of alkali metal fluoride needed to stabilise the lead tetraethyl is readily absorbed by motor fuels owing to its being soluble therein to an appreciable extent. However, in the case of lead tetraethyl alone, or in the case of the usual mixtures of that substance with other organic substances serving to lower the vapour pressure, absorption does not take place to the requisite extent, because the alkali fluorides are practically insoluble in lead tetraethyl. In fact, when the amounts of alkali metal fluoride, considered, in accordance with the former proposal as sufficient, are added to the anti-knock agent itself, decomposition phenomena, due to insufficient solubility of the added stabiliser, will nevertheless make their appearance, during storage under exposure to light, and ultimately result in the mixture becoming thoroughly spoiled.

It has now been ascertained in accordance with the present invention, that the lead tetraethyl can be caused to absorb the amount of alkali metal fluoride required for its stabilisation by maintaining in suspension in the liquid lead tetraethyl or in mixture thereof with other organic compounds serving to lower its vapour pressure

for a considerable period and preferably at elevated temperature, a larger amount of finely dispersed alkali metal fluoride than is directly soluble in the lead tetraethyl. In this manner, the amount of alkali metal fluoride combined by the lead tetraethyl, possibly as an only gradually formed additive compound, can be increased for example, to about ten times the amount absorbed under other conditions and the anti-knock agent can thus be rendered practically light-proof, even when stored for a long time by itself.

The process of the present invention can be carried out in various ways. Good results are already obtained by shaking or stirring the two components of the desired mixture together for some considerable time, for example, several hours, and then separating the liquid anti-knock agent from the undissolved residual alkali fluoride by syphoning or filtration. Better results are however obtained by boiling the lead tetraethyl, or the anti-knock mixture, with an excess of alkali metal fluoride, under a vacuum, in the reflux condenser.

EXAMPLE

1000 cc. of a known anti-knock mixture containing 60% of lead tetraethyl, 30% of dibromoethylene and 10% of monochloronaphtalene, are boiled at 40 - 50°C. in a reflux condenser, for 1 to 2 hours and under a vacuum of 10 to 15 mm. with 10 grams of a mixture of equal amounts of potassium- and sodium fluoride. The liquid is then filtered off from the undissolved sediment. The liquid now contains 0.05% of fluoride. No precipitation due to decomposition of the lead tetraethyl is observable in the anti-knock agent treated in this manner, even after it has been stored for months under exposure to light.

I claim:

1) A process of stabilising lead tetraethyl and anti-knock mixtures containing the same which comprises digesting said lead tetraethyl or anti-knock mixture containing the same with finely dispersed alkali metal fluoride in a quantity exceeding its solubility in said lead tetraethyl or anti-knock mixture, for an extended period of time so as to cause increased dissolution, and then removing the undissolved residue.

2) A process of stabilising lead tetraethyl and anti-knock mixtures containing the same which comprises digesting said lead tetraethyl or anti-knock mixture containing the same with finely dispersed alkali metal fluoride in a quantity exceeding its solubility in said lead tetraethyl or anti-knock mixture, for an extended period of time and at an elevated temperature.

3) A process of stabilising lead tetraethyl and anti-knock mixtures containing the same which comprises subjecting said lead tetraethyl or anti-knock mixture containing the same together with finely dispersed alkali metal fluoride in a quantity exceeding its solubility in said lead tetraethyl or anti-knock mixture to boiling, while condensing the vapours formed and reintroducing the condensate into the boiling mixture, and finally removing the undissolved residue.

4) A process of stabilising lead tetraethyl and anti-knock mixtures containing the same which comprises subjecting said lead tetraethyl or anti-knock mixture containing the same together with finely dispersed alkali metal fluoride in a quantity exceeding its solubility in said lead tetraethyl or anti-knock mixture to boiling at reduced pressure, while condensing the vapours formed and reintroducing the condensate into the boiling mixture, and finally removing the undissolved residue.

5) An anti-knock agent comprising lead tetraethyl in stabilised form containing an alkali metal fluoride in solution in a proportion exceeding the limit of solubility under normal conditions.

HB/Ga/

KE 0000953

DEPARTMENT OF COMMERCE
United States Patent Office
Washington

Hutz & Joslin,
521 Fifth Ave.,
New York, N. Y.

Applicant: Josef M. Michel

Ser. No. 101,080
Filed Sept. 16, 1936
For Process for stabilising
lead tetraethyl and anti-
knock mixtures containing
same.

References cited:

I.G. Farb. (Br.)	414,581	Aug. 9, 1934	44-9.01
(2 sheets)			
Smith, "Introductory to Inorganic Chemistry", 3rd ed.			
(1921) Century Pub. Co. N. Y. (Copy in Div. 59)			
Pages 190-196.			
Jourdan	1,976,564	Oct. 9, 1934	23-32

I. G. Farb. describes broadly the solution of alkali flourides in lead tetraethyl mixtures.

Applicant proposes to dissolve the difficultly soluble salt by using heat, with a reflux to avoid loss of the solvent. Such method of dissolving a relatively insoluble salt by heating the solvent is obvious to anyone familiar with elementary chemistry.

The claims are all rejected as unpatentable over I. G. Farb. taken with Smith showing that most salts are increasingly soluble in solution, with increased temperature, and that careful cooling will allow a supersaturated solution to retain its solute; also taken with Jourdan showing the simple leaching of an inorganic substance by heating the solvent and refluxing the same by contact with a condensing devise - also in contact with an excess of substance to be leached - also having the undissolved residue separated after leaching.

Examiner.

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IN THE UNITED STATES PATENT OFFICE

Josef M. Michel)
Ser. No. 101 080)
Filed Sept. 16, 1936)
For PROCESS FOR STABILIZING)
LEAD TETRAETHYL AND ANTI-)
KNOCK MIXTURE CONTAINING)
SAME.)

Division 64

Room 4708

New York, N.Y.

May 27, 1937.

Hon. Commissioner of Patents.

SIR:-

In response to Office Action dated 4th December 1936, the Examiner is requested to reconsider his rejection of the claims in this case for the following reasons.

The Examiner's position with respect to the claims is understood to be that British Patent Specification No. 414 581 broadly discloses the favourable effect of the presence of alkali fluorides on lead tetraethyl mixtures, and that it would not amount to invention to employ methods generally known to lead to an increased dissolution of difficultly soluble compounds in incorporating alkali fluorides in such tetra-ethyl mixtures.

The general applicability of the information supplied by the Smith and Jourdan publications, is not denied; it is believed, however, that it was not obvious in the present case that the application of the principles laid down in Smith, would lead to an increased solution of alkali metal fluorides in tetraethyl lead at the temperatures of storage, i. e. room temperatures. This is so for the reason that there is nothing to show that the solutions obtained in accordance with the present invention are supersaturated at room temperature. Observations rather tend to show that the capacity of tetraethyl lead for dissolving alkali fluoride, is quite substantial even at room temperature, but that for some reason or other such solution progresses very much more

slowly than in otherwise similar cases. Since usually digestion of a substance of even limited solubility with the dissolving medium at normal temperature leads within a comparatively short time to a substantially saturated solution, it could not be anticipated that the quantities of alkali fluorides which are dissolved by tetraethyl lead within a period of this order, would be only a fraction of the dissolution capacity of tetraethyl lead, which incidentally, of course, was not known. It was only the discovery that by a very prolonged treatment of tetraethyl lead with alkali metal fluorides, resulted in progressively increased proportions of fluorides becoming dissolved, which lead to attempts to shorten the duration of such treatment by the application of higher temperatures as shown in the present specification.

To sum up, it could not be anticipated that the application of the usual means for dissolving difficultly soluble substances in fluids would in the present case result in an appreciable increase of the concentration in respect of the fluoride of the solutions obtained, and it is believed therefore that the application of such known methods with an entirely unobvious and advantageous result merits the grant of a patent.

Respectfully submitted

Attorneys for Applicant

DEPARTMENT OF COMMERCE
United States Patent Office
Washington

Hutz & Joslin
521 Fifth Ave.
New York, N. Y.

Applicant: J. M. Michel

Ser. No. 101,080
Filed Sept. 16, 1936
For PROCESS FOR STABILISING
LEAD TETRAETHYL AND
ANTI-KNOCK MIXTURES
CONTAINING SAME.

Responsive to argument filed May 28, 1937.

The claims are again and Finally rejected as showing no procedure for dissolving a salt other than would be expected of one skilled in the art in view of I. G. Farb. reciting the desirable combination i.e. a solution of alkali fluoride with lead tetra ethyl. Applicant finds that the solvent will not dissolve sufficient salt in the cold state, hence he proposes to heat the solvent. Such solution of the problem, if it is a problem, is obviously elementary, nor does the solution acquire the dignity of invention by reason of the additional proposal to carry out the heating by a conventional extraction, with a refluxing condenser to prevent loss of solvent, or at reduced pressure to prevent decomposition thereof.

Applicant argues that there is no evidence that the solution is supersaturated; that rarely does simple agitation fail to effect solution. Applicant does not know that the solution is not supersaturated, and rarer still does heating fail to enhance the solubility of solute in a solvent, both as to rate of solution and quantity dissolved.

Examiner

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Personal and Confidential

February 11, 1938

Mr. J. H. Schaefer
Ethyl Gasoline Corporation
P. O. Box 688
Wilmington, Delaware

Dear Mr. Schaefer:

Thanks for your letter of February 7th with its further information concerning the use of certain alkali metal fluorides for stabilizing tetraethyl lead. I did not wire you because there seemed to be no point in obtaining further information.

I have just had a letter from Mr. Bevan, asking me when I expect to visit him in England. I have replied that to the best of my knowledge it would probably be in early May. If you now or at a later date have any information which indicates that this date should be moved either forward or backward I would appreciate your letting me know as soon as possible.

Very truly yours,

RAK:is

Robert A. Kehoe, M.D.

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