

**Chapter 1 : Mary Bidwell Breed - Wikipedia**

*Search the history of over billion web pages on the Internet.*

Of those, ester-base oils are favorably used for engine oils for jet planes and automobiles, and for greases, etc. As ester-base oils, there are disclosed various types of esters, such as monoesters to be obtained through reaction of an aliphatic monocarboxylic acid and a monoalcohol; diesters to be obtained through reaction of aliphatic dibasic acid and monoalcohol; esters to be obtained through reaction of polyalcohol and aliphatic carboxylic acid; complex esters to be obtained through reaction of polyol, polybasic acid and aliphatic monocarboxylic acid; etc. Patent References 1 to 5. On the other hand, disclosed is a complex alcohol ester obtained from polyol, polybasic acid or its anhydride and polyalcohol, which is said to have excellent lubricity and biodegradability Patent References 6 to 9. These patent publications have no other substantial description relating to polyalcohol than one relating to alkyl alcohol. In addition, the patent publications say that the product obtained through reaction of the above-mentioned materials contains a polybasic acid ester and a heavy component, but suggest that removing the polybasic acid ester through stripping to give a lubricant oil of high-viscosity heavy component is preferred. The patent publications do not describe detailed analysis of these products.

**Means for Solving the Problems** The present inventors have variously studied for the purpose of solving the above-mentioned problems and, as a result, have considered that when a predetermined group is introduced into the polyol side chain end of polyester, then flexibility could be given to the molecule and the lubricity performance of the obtained complex alcohol ester could be thereby bettered, and have further made various investigations. As a result, the inventors have found that the friction coefficient of a complex alcohol ester composition containing a polyester that has a predetermined group introduced into the polyol side chain end thereof is dramatically reduced as compared with that of already-existing complex alcohol compositions not having the group. Further, regarding the complex alcohol ester composition, the inventors have found a surprising effect that its friction coefficient is almost constant or is rather reduced at the time of temperature increase; and on the basis of these findings, the inventors have completed the present invention. That is, the means for solving the above-described problems are as follows.

**R OH<sub>n</sub>** wherein R represents an n-valent aliphatic, alicyclic or aromatic group, one or more carbon atoms not adjacent to each other in R may be individually substituted with an oxygen atom, and n indicates an integer of 2 or more are linked through at least two ester bonds via at least one molecule of a polybasic acid, and at least a part of the non-linked side chain ends of the polyol have a group represented by a formula II: **AO kR<sub>2</sub>** wherein R<sub>2</sub> represents a hydrocarbon group, A represents a divalent linking group, and k indicates an integer via a polybasic acid. The complex alcohol ester composition according to any one of [3] to [11], wherein the polybasic acid ester that the light component contains is a compound represented by the formula VIb: **R OH<sub>n</sub>** wherein R represents an n-valent aliphatic, alicyclic or aromatic group, one or more carbon atoms not adjacent to each other in R may be individually substituted with an oxygen atom, and n indicates an integer of 2 or more, a polybasic acid or a polybasic acid anhydride, and a monoalcohol represented by a formula III: **HO AO kR<sub>2</sub>** wherein R<sub>2</sub> represents a hydrocarbon group, A represents a divalent linking group, and k indicates an integer of from 1 to 30, and dehydrating and condensing the mixture.

**Advantage of the Invention** The complex alcohol ester composition or the lubricant containing it of the invention has a low friction coefficient, and at the time of temperature increase, the friction coefficient thereof is almost constant or is rather reduced. This property is favorable as lubricant. When the lubricant is used in heat-generating power-system machines, then the energy consumption can be reduced and the fuel cost can be thereby cut.

**Complex Alcohol Ester Composition:** The invention relates to a complex alcohol ester composition containing a predetermined polyester. The composition contains a predetermined polyester as the indispensable ingredient thereof, and preferably contains a light component containing a polybasic acid ester along with the indispensable ingredient. The predetermined polyester is a factor of determining the lubricity of the composition thereof, but it is a solid or a high-viscosity liquid, and therefore, adding a low-viscosity liquid thereto better the usability of the composition as a base oil of a lubricant oil. Preferably, the low-viscosity liquid is a polybasic acid ester that is produced along with the

polyester in the production method of the invention from the viewpoint of the production thereof, to which, however, the invention is not limited. In the complex alcohol ester composition of the invention, the compositional ratio of the high-polymer polyester and the polybasic acid ester-containing light component could be determined through gel permeation chromatography GPC. The polybasic acid ester gives a sharp peak in the GPC pattern thereof and its intensity is high, and therefore the ester can be readily detected. In the complex alcohol ester composition of the invention, the ratio of the polyester to the light component is not specifically defined. Mixing the polyester and the light component betters the lubricity of the composition, which is therefore useful as a lubricant. The ratio could be controlled by controlling the blending ratio of the three starting material in the production method to be mentioned below. By separating the light component through distillation or the like followed by mixing it with the remaining polyester in any desired ratio, the ratio of the components could be controlled to fall within a preferred range. Preferably, the complex alcohol ester composition of the invention is produced by blending the three starting material as mentioned below followed by dehydrating and condensing them; however, two starting materials polyol and polybasic acid or polybasic acid anhydride, or polybasic acid or polybasic acid anhydride and monoalcohol may be first reacted and thereafter with the remaining starting material. The polybasic acid ester contained in the light component and the high-molecular-weight polyester are similar to each other in point of the structure thereof, and therefore the two well mix with each other. In the complex alcohol ester in the invention, in case where the carbon number of R<sub>2</sub> in the side chain AO kR<sub>2</sub> is large concretely, in case where the carbon number thereof is from 14 to 30 or so, one or both of the polyester and the polybasic acid may be solid, and the complex alcohol ester may be solid at room temperature. In such a case, any other liquid compound, especially an oily medium to be mentioned below may be added thereto to give a liquid composition. These are favorably used as lubricant. The polybasic acid ester of the complex alcohol ester in the invention may be isolated by separately producing it through reaction of a polybasic acid and a monoalcohol, or by separating it through distillation, and therefore mixing the thus-isolated liquid polybasic acid ester and the solid complex alcohol ester may give a liquid complex alcohol ester composition. In the polyester that the complex alcohol ester of the invention contains, at least two molecules of a polyol represented by a formula I: In case where two molecules of a polyol represented by the formula I: R OH<sub>n</sub> are linked through two ester bonds via one molecule of a polybasic acid, the compound has a structure of the following formula Y. R represents a monovalent or more multivalent residue derived from the formula R OH<sub>n</sub> by removing at least two OH groups. AO kR<sub>2</sub> via one or more molecules of the polybasic acid in case where they bond via two or more molecules of the polybasic acid, R may further exist between them. Y represents a residue derived from the polybasic acid to be mentioned below by removing two carboxyl groups. The polyester has a group represented by the formula II: AO kR<sub>2</sub> wherein R<sub>2</sub> represents a hydrocarbon group, A represents a divalent linking group, and k indicates an integer, at least in a part of the non-linked side chain ends of the polyol, via a polybasic acid. One example is a partial structure represented by the following formula Z. In the formula, R and Y have the same meanings as those in the above-mentioned formula Y. Preferably, at least one type of the polyester that the complex alcohol ester composition of the invention contains is a polyester having a partial structure of the above-mentioned formula Y. More preferably, the complex alcohol ester composition of the invention contains at least one type of a polyester in which at least three polyols bond to the structure according to the same bonding mode as above. In general, it is known that dehydrating condensation of a polyol and a dibasic acid gives a hyperbranched polyester where the polyol is crosslinked with the dibasic acid and the side chain of the polyester where the end group is not covalent-bonded is left unreacted OH or forms COOH through reaction with the dibasic acid Non-Patent Reference: Journal of Polymer Science: Polymer Chemistry, p. The main chain of the polyester in the invention is the hyperbranched polyester of the type, and is characterized in that at least a part of the non-linked side chain ends of the polyol has the group represented by the formula II: It is considered that introducing the group of the formula II into a part of the side chain ends of the polyol in the polyester could better the lubricity of the polyester. The polyol moiety of the polyester is represented by the formula I: In the formula, R represents an n-valent aliphatic, alicyclic or aromatic group, one or more carbon atoms not adjacent to each other in R may be individually substituted with an oxygen atom, and n indicates an

integer of 2 or more. In the formula, n is preferably 3 or 4, or that is, preferred is a triol or a tetraol. In the formula, R is preferably an n-valent aliphatic group having from 2 to 20 carbon atoms more preferably from 2 to 15, even more preferably from 2 to 10, still more preferably from 2 to 7, especially preferably from 3 to 5 carbon atoms. However, the invention is not limited to the range; and depending on the use of the composition, preferably, the carbon number may be rather larger. In the aliphatic group. Examples of the polyol represented by the formula I include the following compounds, to which, however, the invention is not limited. There are mentioned diols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,3-butanediol, 1,6-hexanediol, 1,4-dimethylolcyclohexane, neopentyl glycol; triols such as trimethylolmethane, trimethylolpropane, trimethylolbutane, glycerin; tetraols such as pentaerythritol; multiols such as dipentaerythritol, tripentaerythritol; sugar alcohols such as xylitol, sorbitol, mannitol, erythritol, maltitol, isomaltose, arbutin, ribitol, iditol, volemitol, periseitol; sugars such as glucose, etc. Of those, preferred are neopentyl glycol, trimethylolpropane, trimethylolbutane, glycerin, pentaerythritol, dipentaerythritol, and xylitol; more preferred are trimethylolpropane, trimethylolbutane, glycerin, pentaerythritol, and dipentaerythritol, etc. These may be not necessarily high-purity products, but so-called industrial-use brands may be preferably used here. Polybasic Acid or Polybasic Acid Anhydride: As the polybasic acid ingredient of the polyester, preferred is a compound having multiple COOHs in one molecule. Above all, preferred is a dibasic acid; more preferred is a dibasic acid where two COOHs are linked via a linear or cyclic, divalent saturated or unsaturated hydrocarbon group therebetween; and even more preferred is a dibasic acid where two COOHs are linked via an alkylene group. Preferred examples of the dibasic acid include a dibasic acid where two COOHs are linked via an alkylene group having from 1 to 8 carbon atoms more preferably from 1 to 6 carbon atoms therebetween or that is, a compound represented by  $C_yH_{2y}COOH_2$ , in which y indicates a number of from 1 to 8 more preferably from 1 to 6. Examples of the polybasic acid include the following compounds, to which, however, the invention is not limited. The compounds include terephthalic acid, phthalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, trimellitic acid, dimer acid, dimer acid hydrogenate, etc. Of those, preferred are succinic acid, adipic acid, sebacic acid, dimer acid, and dimer acid hydrogenate; and more preferred are succinic acid, adipic acid, and dimer acid. The polybasic acid anhydride is, for example, a product produced through intramolecular or intermolecular dehydrating condensation of two COOHs in the above-mentioned polybasic acid. This is usable here in place of the polybasic acid. Preferred embodiments of the anhydride are the same as mentioned above. Examples of the anhydride include succinic anhydride, glutaric anhydride, adipic anhydride, maleic anhydride, phthalic anhydride, najic anhydride, methylnajic anhydride, hexahydrophthalic anhydride, and mixed polybasic acid anhydrides. Of those, preferred are succinic anhydride, adipic anhydride, maleic anhydride, phthalic anhydride, etc. Side Chain of Polyester: As described above, the polyester is characterized by having the group represented by the formula II:  $AO_kR_2$  in at least a part of the side chain ends of the polyol. In the formula II,  $R_2$  represents a hydrocarbon group, A represents a divalent linking group, and k indicates an integer of from 1 to In the above formula,  $R_2$  is preferably a hydrocarbon group having from 1 to 30 carbon atoms, more preferably an alkyl group having from 1 to 30 carbon atoms, even more preferably from 1 to 25 carbon atoms, still more preferably from 1 to 20 carbon atoms. Of those, when  $R_2$  is an alkyl group having from 1 to 6 carbon atoms, especially a methyl group or an ethyl group, the composition is favorably used as a base oil. In the above formula, k indicates an integer of from 1 to 30, preferably from 1 to 25, more preferably from 1 to 20, even more preferably from 1 to Preferred examples of the group represented by the above formula II include the following that indicates the formula II wherein A is an alkylene group having from 1 to 6 carbon atoms,  $R_2$  is an alkyl group having from 1 to 8 carbon atoms, and k is an integer of from 1 to 3. Specifically, preferred examples of the group represented by the formula II include the following groups. In the following formulae, k has the same meaning as k in the formula II, and the preferred range thereof is also the same as that of the latter. In the following formula, z is a number of from 1 to 30 preferably from 1 to 25, more preferably from 1 to The presence of  $AO_kR_2$  in the side chain of the polyester in the invention is self-obvious in consideration of the production mechanism of the polyester. However, it is difficult to determine the matter as to whether or not  $AO_kR_2$

could be derived from the starting alcohol or polybasic acid ester through spectrometry. In this, when AO kR2 could be detected through spectrometry, then it demonstrates the presence of the side chains in the polyester. In the side chains of the polyester in the invention, it is needless to say that the unreacted OH in the polyol may remain, or the OH in the polyol may react with a polybasic acid or polybasic acid anhydride to form COOH existing therein. However, in case where OH or COOH remains in the polyester in the invention, the hydroxyl value and the acid value of the polyester may increase, which may be often unfavorable in some uses for example, in use for lubricant. A polyester having OH remaining in the side chain therein may be once formed and then at least a part of OHs may be acylated to give the polyester for use in the invention. Specifically, preferred examples of the polyester include a polyester having a group represented by the above-mentioned formula II and also OCOR1 in at least a part of the polyol side chain ends thereof. In this, R1 represents an alkyl group having from 1 to 10 carbon atoms, or an aryl group, preferably a methyl group, an ethyl group, a butyl group or a phenyl group, more preferably a methyl group or a phenyl group, even more preferably a methyl group. Reducing the hydroxyl value through the acylation is favorable from the viewpoint that the polyester can be more readily mixed with any other oily medium. For reducing the acid value of the polyester for use in the invention, a treatment of removing COOH may also be employed. Specifically, examples of the polyester include a polyester in which a part or all of COOHs formed through reaction of the OH in a polyol with a polybasic acid or a polybasic acid anhydride are esterified. For example, the polyester may be one having COOCH3 or the like as esterified through treatment with diazomethane or the like. For example, in case where the polyol is pentaerythritol, there may exist 0, 1, 2, 3 or 4 OHs that ester-bonding therein; and the chemical shift of these quaternary carbons separates at around 40 ppm.

**Chapter 2 : Mesitylene | Revolv**

*Note: Citations are based on reference standards. However, formatting rules can vary widely between applications and fields of interest or study. The specific requirements or preferences of your reviewing publisher, classroom teacher, institution or organization should be applied.*

What is claimed is: The process according to claim 1, wherein the aliphatic alcohol is at least one lower alcohol having 1 to 8 carbon atoms selected from methanol, ethanol, propanol, butanol, hexanol and octanol. The process according to claim 1 wherein the aliphatic alcohol is at least one polyhydric alcohol selected from ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, trimethylolpropane and neopentyl glycol. The process according to claim 1 wherein the aromatic hydrocarbon-formaldehyde resin is selected from xylene-formaldehyde resin and mesitylene-formaldehyde resin. The process according to claim 1 or 5 wherein the modified aromatic hydrocarbon resin has an acid value of 10 to 15. The process according to claim 1 or 5 wherein the water is introduced in the form of steam. The process according to claim 1 or 5, wherein the aliphatic alcohol is a monohydric alcohol having 1 to 8 carbon atoms or a polyhydric alcohol. More particularly, the invention relates to a process characterized in that water or water and an aliphatic alcohol is made present in the reaction system during the reaction and the reaction is made to proceed while removing the formaldehyde formed by the reaction. It has hitherto been widely known that a modified aromatic hydrocarbon resin, which may be hereinafter referred to briefly as "modified resin", can be produced by reacting an aromatic hydrocarbon-formaldehyde resin with an unsaturated polybasic acid or an anhydride thereof such as maleic acid or maleic anhydride. This modified resin may be also regarded as a modified unsaturated polyester, which may be dissolved in monomers such as styrene to be used for purposes similar to those of conventional unsaturated polyester resin. In case, however, an aromatic hydrocarbon-formaldehyde resin, e. It was proposed to use a specified amount of the unsaturated dibasic acid or an anhydride thereof in order to overcome the difficulty see Japanese Patent Publication No. Although the gelation can be fairly prevented by the proposed method, the cured product has a low crosslinking density and insufficient mechanical strength. Therefore, the modified resin as above-mentioned is not satisfactory for use as a resin for fibre reinforced plastics FRP in particular. In order to obtain a modified resin suitable to the use as the resin for FRP in particular, we have studied processes for its preparation carefully and found that the gelling tendency in the final period of the reaction and the low reactivity of the modified resin obtained according to the proposed method are due to the formaldehyde formed in the course of reaction. It might be sufficient if the formaldehyde formed by the reaction is not made present in the reaction system, but it is undesirable to discharge the gaseous formaldehyde into the atmosphere, since it contaminates the working environment. Furthermore, in case a discharge pipe, or the like is employed, such measures would also be unfavorable since the formaldehyde deposits on the inside wall of the pipe and clogs the pipe. Thus, any of the cases is not satisfactory for the commercial practice. An object of the present invention is to provide a modified aromatic hydrocarbon resin having high reactivity with monomers, and further to provide a cured product having superior mechanical strength and resistance to water and alkalis. Another object of the present invention is to provide a process for the preparation of a modified aromatic hydrocarbon resin wherein the reaction of an aromatic hydrocarbon-formaldehyde resin with an unsaturated polybasic acid or an anhydride thereof and if desired, with a saturated polybasic acid or an anhydride thereof, proceeds smoothly and efficiently without causing any gelation during the reaction. The present invention relates to a process for the preparation of a modified aromatic hydrocarbon resin by reacting an aromatic hydrocarbon-formaldehyde resin with an unsaturated polybasic acid or an anhydride thereof, if desired, with a saturated polybasic acid or an anhydride thereof, wherein the improvement comprises making water or water and an aliphatic alcohol present in the reaction system, and carrying out the reaction, while removing formaldehyde formed by the reaction to the outside of the reaction system. In the present invention, although water may be placed in the reactor prior to the reaction, it is preferable to introduce water into the reactor in the form of steam during the reaction. Of course, the foregoing both measures may be taken at the same time. Accordingly, it is possible to

complete the reaction efficiently and smoothly. The modified resin prepared by the process of the present invention is readily soluble in monomers such as styrene, and its curing properties are similar to those of conventional unsaturated polyester resins. The cured product obtained from the modified resin of the present invention far exceeds the conventional unsaturated polyester resins in corrosion resistance, and resistance to water and alkalis. The term "aromatic hydrocarbon-formaldehyde resins" used herein means those obtainable by reacting an aromatic hydrocarbon compound, e. Examples of the unsaturated polybasic acid or an anhydride thereof to be used in the process of the present invention include maleic anhydride, maleic acid, fumaric acid and itaconic acid, and preferably maleic anhydride. Examples of the saturated polybasic acid or an anhydride thereof to be used include adipic acid, sebacic acid, phthalic anhydride, isophthalic acid and terephthalic acid, all of which are used for the preparation of conventional unsaturated polyester resins. In the process of the present invention the amount of water or water and an aliphatic alcohol to be made present in the reaction system should be not less than 5 parts by weight per parts by weight of the aromatic hydrocarbon-formaldehyde resin, and 20 to 35 parts by weight are usually used in consideration of the time, etc. In case water is introduced in the form of steam, the above-mentioned quantity in terms of the weight of condensed water may be used. In case an aliphatic alcohol is used together with water, the ratio of alcohol to water is not specifically limited, but in general the alcohol is used in a quantity a little less than or approximately equal to that of water. Examples of aliphatic alcohols to be used in the present invention include monohydric alcohols having 1 to 8 carbon atoms such as methanol, ethanol, propanol, butanol, hexanol and octanol; polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol; and trimethylolpropane, neopentyl glycol, etc. The present invention will be described, referring to xylene-formaldehyde resin as an example of the aromatic hydrocarbon-formaldehyde resin. As the reaction proceeds, part of the acetal and formal bonds in the resin are broken to form formaldehyde, which readily dissolves in the water present in the reaction mixture. The resulting modified resin shows an acid value of 10 to 40, and is dissolved in styrene in the presence of a polymerization inhibitor. If more than 35 parts by weight of maleic anhydride are added, the quantity of acid exceeds the performance of the xylene-formaldehyde resin at which the acid is consumed, and the acid value of the resulting modified resin is not reduced down to a desired value. If the quantity is less than 10 parts by weight the cured product shows poor physical properties. In the foregoing description, xylene-formaldehyde resin and maleic anhydride have been used as specific examples of reactants, but similar results can be obtained when other aromatic hydrocarbon-formaldehyde resins are used, for example, toluene-formaldehyde resin, mesityrene-formaldehyde resin, benzene-formaldehyde resin and styrene-formaldehyde resin, or other unsaturated dibasic acids than maleic anhydride are used. Similar results can be also obtained, when a saturated polybasic acid is further added, if necessary. The modified resin prepared according to the process of the present invention is dissolved in monomers such as styrene, vinyltoluene and diallyl phthalate, and the resulting solution can be easily cured in the presence of organic peroxides such as benzoyl peroxide, methylethylketone peroxide and ditertiary-butyl peroxide as catalyst in the same manner as in the case of the conventional unsaturated polyester resins. The curing characteristics of the present resin are similar to those of the conventional unsaturated polyester resins, and the cured product has a high resistance to corrosion, and to water and alkalis in particular, and has excellent adhesiveness and electrical properties. The modified resin prepared according to the process of the present invention can be used as corrosion-resistant FRP, gel coat, insulating varnish, primer and moulding resin. Several examples will be given below to illustrate the invention further, where "parts" and "percents" are by weight unless otherwise specially mentioned. EXAMPLE 1 A hundred parts of xylene-formaldehyde resin, 22 parts of maleic anhydride and 22 parts of water were introduced into a reactor provided with a stirrer, a thermometer, a reflux condenser and a formaldehyde distilling device. The modified resin thus obtained was dissolved in 73 parts of styrene containing ppm of hydroquinone. The resulting solution will hereinafter be referred to as "resin A ". Thereafter, the reaction was continued for 5 hours, and thus parts of a modified resin having an acid value of 26 was obtained. The resulting resin was dissolved in 78 parts of styrene containing ppm of hydroquinone. The resulting solution will be hereinafter referred to as "resin B ". During the reaction, sublimation of paraformaldehyde took place

vigorously and the smell of formaldehyde was noticed. The resulting resin was dissolved in 73 parts of styrene containing ppm of hydroquinone. The resulting solution will be hereafter referred to as "resin C ". The "double bond content" was determined for each of the modified resins prepared in Examples 1 and 2 and the Comparative Example according to infrared absorption spectrum method, and their "double bond equivalent" was calculated from the "double bond content". The "theoretical double bond equivalent" was also calculated for each of the resins. Thereafter, the "percentage of retained double bond" was calculated as a ratio of the theoretical equivalent to the observed one. The results are shown in the following table.

**Chapter 3 : The polybasic acids of mesitylene. - CORE**

*The Polybasic Acids Of Mesitylene () [Mary Bidwell Breed] on www.nxgvision.com \*FREE\* shipping on qualifying offers. This scarce antiquarian book is a facsimile reprint of the original.*

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Usage guidelines Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying. We also ask that you: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help. Please do not remove it. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. You can search through the full text of this book on the web at <http://www.nxgvision.com>. It is proposed to publish these monographs in Separate numbers at irregular intervals as material is accumulated. The numbers will be combined into volumes of about pages. Carey Thomas, , ex-officio. Of the acids theoretically possible, the most interesting are those derived from mesitylene and the durenes by the introduction of carboxyl groups in place of the hydrogen of the nucleus. In the case of these hydrocarbons, however, only one carboxyl group has so far been introduced. Of the sixteen possible acids derived from mesitylene by successively replacing ring hydrogen atoms with carboxyl groups and subsequently oxidizing the various methyl groups, only five are known. The object of the following investigation was to prepare and study the three acids derived from mesitylene by replacing the hydrogen atoms of the nucleus with one, two, and three carboxyl groups. Historically, mesitylene carbonic acid is interesting as the substance whose failure to give an ester when treated with alcohol and hydrochloric acid, first led to a systematic study of di-ortho-substituted compounds and their peculiarities. Di-ortho-substituted nitriles are, in general, very difficult to saponify. For example, "o, o, di-iodo-benzoyl chloride can be boiled with sodium hydroxide solution without much decomposition. Many other carboxyl compounds, such as mixed ketones, when di-ortho-substituted, exhibit an inertness similar to the acids and nitriles. Instead, the ketone group is split off, leaving a hydrocarbon. Meyer, *Berichte*, 27, ; Sudborough, *Journ. Soc.*, 71, , " *Berichte*, 28, ; 29, Meyer explained as a result of the space arrangement of the molecule. This inertness of the di-ortho-substituted group is evident not only in its indifference to reagents, of which cases have been cited above, but also in the comparatively small effect which the presence of such a group has on the molecule as a whole. Certain well-known peculiarities of mesitylene, for instance, can be explained as the effects of di-ortho-substitution, such as the ease with which two or three groups like the nitro group are introduced. One nitro group goes easily into benzene, but once there it makes the introduction of a second group more difficult; while in mesitylene the first nitro group has so little inhibiting effect that it is practically impossible to stop nitration at the point where only one group has entered. A more remarkable example of this is that although only one acyl group can be introduced into benzene, toluene and other hydrocarbons, by the action of an acyl chloride and aluminium chloride, two such groups can be introduced into mesitylene, durene and isodurene by the same reaction. In the case of mesitylene, it has been found that even a third group can be introduced by sufficiently energetic means. But as yet no one has succeeded in introducing three aliphatic acyl groups into mesitylene. This account of di-ortho-substitution effects shows that, if the three methods available for introducing carboxyl groups into "Baum and V. Meyer, *Berichte*, 25, ; V. Meyer, *Berichte*, 29, and Di-ortho-substitution is in these methods a hindrance, while in the third method it is a help. It favors the introduction of acyl groups to form the necessary ketones and does not interfere with oxidation of these ketones to the desired acids. This last method was, therefore, selected for preparing the acids of mesitylene. In selecting the acid chlorides suitable for the purpose, benzoyl chloride could not be considered, as Louise"

showed that the oxidation of benzoyl mesitylene gave o and p benzoyl mesityl- enic acids; and Mills and Easterfield" on oxidizing di-benzoyl mesitylene got two dibenzoyl uvitic acids. An aliphatic acyl group was therefore necessary, and acetyl and chloracetyl chlorides were used. Soc, 15, 22; Chem. To obtain the diketone in a solid state, the following method has proved highly satisfactory: One part one molecule of mesitylene is dissolved in from ten to fifteen parts by weight of carbon disulphide in a flask provided with a dropping funnel and a return condenser. Six parts by weight of fresh, finely powdered aluminium chloride is added, and then two parts about three molecules of acetyl chloride is allowed to run slowly through the dropping funnel, with an interval of 24 hours between the first and last portions added. If the alum- inium chloride is added last, its action on the excess of acetyl chloride present results in relatively large amounts of bye-pro- ducts such as acetylacetone, and some of the mesitylene is either left unchanged or converted merely into its mono-acetyl deriva- tive. The flask, after all the acetyl chloride has run in, is set in the direct rays of the sun, and left to itself for a length of time depending on the weather. In bright winter weather two weeks is a fair average time. The action of sunlight at first accelerates the evolution of gas and finally conditions it absolutely. When no further action is observed in ordinary sunlight, the upper, clear layer of the solvent is poured off and saved for future syntheses. The dark, viscous mass remaining is removed from the flask, and dropped in small portions on cracked ice. The usual method of adding ice to the mixture in the flask is not to be recommended in this case, on account of the large excess of aluminium chloride. The oil obtained by decomposition with the ice water, is ex- tracted with successive portions of ligroine ; the solvent is allowed to evaporate over night and deposits long needles of di-acetyl mesitylene. Once in possession of the solid no difficulty is experienced in purifying even very impure products. In the literature of the subject, there is no record of any attempt to introduce three acetyl groups into mesitylene. It has been found that in experiments where a great excess of acid chloride and aluminium chloride were used, only diketone was obtained. In fact, one very good way to make di-acetyl mesitylene is to dissolve aluminium chloride in acetyl chloride, and drop in mesitylene. On standing in sunlight, crystals of the diketone separate from the liquid, but no triketone has been obtained. Raising the temperature favors the formation of acetylacetone and consequent waste of the acid chloride. It is possible that very prolonged action of sunlight might have the desired result, as one mixture made up in the usual way, after standing for two months in a window facing southwest, was observed to give off gas slowly when the atmosphere was unusually clear. But even if the complete transformation of mesitylene into tri-acetyl mesitylene were possible by this means, the synthesis would require so long a time that it was desirable to seek some other and shorter method for forming a triketone. Collet," and is a solid melting at One part one molecule of mesitylene, three parts about two and a half molecules of chlor- acetyl chloride, fifteen parts of carbon disulphide and six parts of aluminium chloride are mixed usually in the order given in a flask that is kept cool with running water. The mixture may be heated at once on a water bath for one or two hours, when the reaction is complete; or it may be left in the cold for 48 hours or more. The solvent is poured off and the product of the reac- tion decomposed with ice in the same way as di-acetyl mesitylene. The diketone comes out as a grayish solid which is filtered off and washed with dilute hydrochloric acid. From 45 grams of mesityl- ene, grams of the crude product were gotten. This always contains traces of chloracetophenone, which in one synthesis was gotten in sufficient quantity to be analyzed and identified. The residue, after extracting twice with ligroine, is crystallized from hot alcohol, from which it comes out in well-formed plates. The last trace of coloring matter and of the odor of chloracetophenone is removed only by boiling the alcoholic solution with animal charcoal. Ether dissolves 26 parts per , and on evaporating leaves it in transparent crystals mm. The diketone is insoluble in water, nearly insoluble in ligroine, easily soluble in benzene, acetone and other organic solvents. It also dissolves in concentrated sulphuric and nitric acids in the cold, and ia reprecipitated unchanged when the solutions are diluted with water. Like other di-ortho-substituted diketones, di-acetyl mesitylene gives no oxime, hydrazone or acid sulphite addition product. On the other hand, contrary to the observation of Klages" that di- ortho-substituted ketones are converted into hydrocarbons by syrupy phosphoric acid, this diketone, heated with phosphoric acid, does not give mesitylene. An excess of syrupy phosphoric acid and 5 grams of the diketone was heated in a flask with a return condenser. After heating for sev- eral hours, some of the mixture was diluted and subjected to dis-

tillation with steam. No mesitylene or any other volatile substance was obtained. Klages obtained mesitylene from di-acetyl mesitylene. The diketone was recovered unchanged. Though di-acetyl mesitylene is a perfectly neutral substance, di-chloroacetyl mesitylene, probably on account of the chlorine atoms next its carboxyl groups, possesses very weak acid properties. It dissolves in alcoholic caustic potash with a deep red color, and water, which precipitates it from its solution in ordinary alcohol, does not precipitate it from the alkaline solution. It gives, however, no color reaction with ferric chloride. Meyer" suggested that di-acyl mesitylenes, which are necessarily diketones, might give condensation products analogous to those obtained by Knoevenagel and others from open chain diketones. Iodine in alcoholic potash, hydroxylamine, alcoholic ammonia, finely divided silver, metallic sodium in absolute ether, aniline, etc. The ketone was recovered unchanged in most cases, but in others oily or tarry decomposition products were obtained. Attempts to prepare tri-chloroacetyl mesitylene. In a second experiment, 0. This was then added to a hot solution of 1 gram di-chloroacetyl mesitylene in carbon disulphide and the whole heated on a water bath for several hours. A small amount of tarry decomposition product was formed. Chloroacetyl chloride was next used as a solvent, both on account of its relatively high boiling point and its holding the addition product of the acyl chloride and aluminium chloride in solution. When mesitylene is added to a solution of aluminium chloride in chloroacetyl chloride, crystals of di-chloroacetyl mesitylene separate out in the cold, but no tri-chloroacetyl derivative is gotten. When di-chloroacetyl mesitylene is heated with the solution the main product is a thick black oil, which can not be made to solidify. Some of the diketone is recovered unchanged. The action of sunlight was tried on a mixture of mesitylene and the corresponding reagents made up in the usual way, but with a large excess of chloroacetyl chloride. The effect was much less than in the case of acetyl chloride; the evolution of gas was slower and ceased altogether after about two months. COOH CH<sub>3</sub> acetyl mesitylene was weighed out in portions of 10 grams each into 4-litre bottles, which contained each a solution of 31 grams potassium permanganate and 17 grams potassium hydroxide in 4 litres of water. The bottles were stoppered and shaken frequently. Oxidation began at once and after 48 hours the solution was usually colorless, while a heavy precipitate of manganese di-oxide had formed.

**Chapter 4 : American Chemical Journal,**

*Excerpt from The Polybasic Acids of Mesitylene Several instances of abnormal behavior in di-ortho-substituted compounds had been recorded before this work of Meyer's, but he first pointed out the cause, and laid down the general principle that di-ortho - substitution profoundly affects the reactivity of any group.*

The use of nitric acid as a chemical oxidant for the production of aromatic carboxylic acids has been known for many years and has been used commercially to some extent. The major objection, however, to the use of nitric acid as a chemical oxidant for the production of aromatic carboxylic acid is cost, for to sheet the desired oxidation reaction large quantities of nitric acid are required. Moreover, in addition to the cost involved in the use of nitric acid in reagent amounts, the method invariably results in low yields of desired product along with difficultly extractable intermediates and by-products. It has now been discovered that good yields of the desired polycarboxylated compounds can be obtained if a feedstock consisting essentially of an alkyl substituted aromatic acid is oxidized in the liquid phase with a free oxygen-containing gas at temperature of about to C. The amount of the hydrogen chloride-nitric acid catalyst provided in the present invention can vary over a wide range with no particular limits being critical and is effective in the absence of catalytic metals such as cobalt. The preferred molar ratio of hydrogen chloride to nitric acid in the catalyst of the present invention is about 1: The alkyl substituted aromatic feedstock to be oxidized can contain only one lower alkyl radical or it can contain a plurality of lower alkyl radicals, if desired. Also the presence of the carboxyl radical need not be limited to one but a plurality thereof can be provided. Although the methyl radical is preferred, the alkyl substituent can be other non-tertiary structures such as ethyl, propyl, isopropyl, n-butyl or isobutyl 2-methyl propyl. Aromatic acid feedstocks having a tertiary butyl substituent, however, are not favored for the results produced are not found advantageous. Thus, the feedstock can contain from one to live alkyl groups and one to five carboxyl groups but, of course, the total number of alkyl and carboxyl radicals is not more than six. Representative acids which can be oxidized in accordance with the present invention can be enumerated as follows: For example, an alkyl substituted benzene such as xylene can be conveniently oxidized to toluic acid in the presence of molecular oxygen by the use of a catalyst such as cobalt toluate, cobalt naphthenate, etc. The other partially carboxylated alkyl substituted aromatic acids can be similarly derived from their corresponding alkyl substituted benzenes. In order to obtain the desired yields of the polybasic acids in a high state of purity in accordance with the present invention it is preferred to conduct the oxidation reaction in a medium which effects the solubilization of the reactants. Suitable medias are solvents selected from the group consisting of Water, stable solvents such as acetic acid or other polar organic solvents, or mixtures of these materials. Although the use of any of the above solvents is effective, we have found that it is particularly advantageous to use water or a combination of the stable organic solvents and water; the water seemingly serving as an activator to assist in carrying the feedstock all the way to the desired polycarboxylated compound, for example, oxidizing all methyl groups to carboxyl groups. Advantageously, when in admixture with the other solvents the water should be present in concentrations of at least about 10 percent by weight based on the acid feedstock with the upper concentration of the water being limited only by recovery problems. For example, the water can be present in amounts up to percent or more if desired. The total amount of solvent present in the system can vary over a wide range and is usually provided in amounts sufficient to solubilize a substantia amount of the organic acid feedstock and the catalyst. The amount of solvent will, therefore, depend on the choice of solvents and the solubility of the particular acid feedstock in the solvent. Furthermore, the solvent need not be present in amounts sufficient to solubilize the entire charge of acid feedstock but enough solvent must be present to provide a sufficient amount of the acid in solution in order to effect the oxidation, with additional amounts of the acid being solubilized as the reaction products are formed. Generally, the solvent will be present in amounts ranging from about 25 to 2, percent by weight of the acid feed and preferably about to percent by weight. The conversion in such a system will generally be complete after contact periods ranging from about 0. The present invention can best be illustrated by the following specific examples. Heat was applied and a temperature or" about C. The reaction was controlled at this

temperature for about 2 hours. At the end of this time, the bomb of the alkylated aromatic acid oxidized is noted below. However, when the two acids are combined in the same molar ratio as was used in Examples 1 and 2 a high conversion yield of terephthalic acid is obtained. This clearly illustrates the advantages of employing the catalyst of the present insystem is operative in an organic solvent as well as in water which is the preferred solvent. Example 7 illustrates that toluic acids other than p-toluic acid are suitable feeds for the present invention and Example 8 shows that aromatic acids other than the toluic acids are also suitable feeds for the present invention. It should also be noted that the conversion yield is expected to be higher in a reaction sys tem in which better contact of the oxygen with the liquid phase is obtained than that realized in the exacting laboratory equipment. A method for the preparation of polycarboxylic acid which comprises oxidizing with molecular oxygen and with a pressure suficient tomaintain the liquid phase, an alkylbenzene carboxylic acid having 1 to 3 alkyl radicals, the alkyl radicals having 1 to 3 carbon atoms, at a temperature of about to C. The method of claim 1 in which the solvent is water. The method of claim 1 wherein the alkyl radical is methyl. The method of claim 4 wherein the solvent is water. The method of claim 4 wherein the solvent is acetic acid.

**Chapter 5 : Full text of "The polybasic acids of mesitylene"**

*The polybasic acids of mesitylene. By Mary Bidwell Breed. Abstract. Caption [www.nxgvision.com](http://www.nxgvision.com) of access: Internet Topics: Mesitylene.*

A method of conducting a paired electrochemical synthesis reaction which comprises the steps of: The method of claim 1 wherein the chemical reaction between said higher valence oxidizing state ions of the regeneratable redox reagent and said organic substrate is conducted in a reaction zone outside the electrochemical cell, said method including the step of separating said organic compound from the spent redox reagent before returning said spent redox reagent to the anolyte compartment for regeneration. The method of claim 2 wherein the electrochemical cell is equipped with a stable cation exchange membrane. The method of claim 5 wherein the stable cation exchange membrane is a fluorinated ion exchange membrane. The method of claim 5 including the step of adding to the anolyte sufficient strong acid to inhibit passage of the regeneratable redox reagent from the anolyte to the catholyte compartments. The method of claim 8 wherein the ratio of the molar hydrogen ion concentration of said strong acid in the anolyte compartment is greater than the total molar concentration of positively charged ions of said regeneratable redox reagent. The method of claim 8 wherein the pH of the anolyte comprising said strong acid solution is less than about 1. The method of claim 5 wherein the catholyte includes a metal ion complexing agent. The method of claim 2 wherein the membrane divided electrochemical cell is a three compartment cell comprising a central compartment positioned between anolyte and catholyte compartments. The method of claim 13 wherein at least one membrane of the said three compartment cell is a stable fluorinated anion exchange membrane. The method of claim 13 wherein both membranes of said three compartment cell are stable cation exchange membranes, and the anolyte side membrane is fluorinated. The method of claim 13 wherein both membranes of said three compartment cell are stable anion exchange membranes, and the anolyte side membrane is fluorinated. The method of claim 2 wherein the electrochemical cell is equipped with a stable anion exchange membrane, a catholyte containing the salt of an acid with an oxidation stable anion, and includes an oxidation stable acid added to the catholyte to maintain the pH of the catholyte in the range from about 5 to about 8. The method of claim 17 wherein the anion of the oxidation stable acid is a member selected from the group consisting of sulfate, bisulfate, phosphate, methanesulfonate, fluoride, tetrafluoroborate and hexafluorophosphate. The method of claim 17 wherein oxidation stable acid accumulating in the anolyte is recovered and recycled to the catholyte. The method of claim 17 wherein the stable anion exchange membrane is a fluorinated type. The method of claim 2 wherein the membrane of the electrochemical cell is a stable bipolar type. The method of claim 21 wherein the stable bipolar membrane is a fluorinated type. The method of claim 2 wherein the higher valence state oxidizing ion of said regeneratable redox reagent is reacted with an oxidizable aromatic compound. The method of claim 23 wherein the oxidizable aromatic compound is benzene, naphthalene or anthracene and the product formed is the corresponding quinone. The method of claim 23 wherein the oxidizable aromatic compound is p-xylene, p-toluic acid, p-hydroxymethyl toluene, p-hydroxymethylbenzaldehyde or 1,4-dihydroxymethylbenzene and the product formed is terephthalic acid. The method of claim 25 including the step of condensing the terephthalic acid with ethylene glycol produced from the catholyte of the electrochemical cell to form polyethylene terephthalate. The method of claim 23 wherein the oxidizable aromatic compound is m-xylene which is oxidized to isophthalic acid, and the isophthalic acid is condensed with ethylene glycol produced from the catholyte of the electro-chemical cell to form polyethylene isophthalate. A method of making polyesters in a paired electro-chemical synthesis reaction, which comprises the steps of: The method of claim 28 wherein the polybasic acid formed is a member selected from the group consisting of terephthalic acid, isophthalic acid, trimesic acid, naphthalene-1,4-dicarboxylic acid and an aliphatic acid of the formula  $\text{HOOC}-\text{CH}_2\text{-n-COOH}$  wherein n is a number from 2 to The method of claim 29 wherein the polyester formed is polyethylene terephthalate or polyethylene isophthalate. **BACKGROUND OF THE INVENTION** The present invention relates generally to methods of conducting paired synthesis reactions electrochemically, and more specifically, to the preparation of ethylene glycol at the cathode of an

electrochemical cell while simultaneously producing a regeneratable redox reagent at the anode of the same cell, which redox reagent can be reacted with an organic substrate to prepare a secondary product indirectly. Ethylene glycol is a major industrial chemical with worldwide production of about 20 billion pounds per year. Ethylene glycol is widely used in manufacturing polyester films and fibers and as an automotive coolant and antifreeze. The major source of ethylene glycol is from epoxidation of ethylene which is derived from petroleum, followed by hydration to form the glycol. However, dwindling petroleum reserves and petroleum feedstocks coupled with escalating prices has led to development of alternative routes based on syngas. Representative processes are described in U. In a recent patent to N. Significant effort has been made to improve the economics for the electrochemical synthesis of ethylene glycol. One such example is found in U. That is, the U. Accordingly, the present invention contemplates even more economically attractive electrochemical synthesis reactions with the simultaneous production of ethylene glycol wherein two or more useful products are generated simultaneously at the anode and cathode of the same electrochemical cell, and where the anode products are formed indirectly, hereinafter referred to as "paired electrochemical synthesis". The process is specially significant in light of the paired products ability to share in capital costs for cells, as well as operating costs, and particularly power. But, the process is also quite surprising in view of the fact that usually paired reactions cannot be conducted successfully side-by-side in the same electrochemical cell due to fundamental incompatibilities in cathodic and anodic reactions, e. In the absence of sufficient protons a pH imbalance occurs on the cathode side. This will depress the conversion efficiency of formaldehyde to ethylene glycol which translates into greater power consumption and costs per unit of product produced. In addition, passage of these metal ions of regeneratable redox reagents from the anode to the cathode side, has a tendency to inhibit the electroreduction of formaldehyde to ethylene glycol by "poisoning" the carbon cathode. Consequently, the hydrogen current efficiency increases and the desired ethylene glycol current efficiency of at least 70 percent decreases. Membranes are also subject to destruction by oxidants formed in the anolyte. Moreover, back-transfer of catholyte species, particularly organics, such as formaldehyde, ethylene glycol and oxidizable electrolyte anions, such as formate, into the anolyte causes deactivation of oxidant species and current efficiency losses. Accordingly, the present invention provides for important technical improvements in the electrochemical production of ethylene glycol making this method even more economic through a paired reaction format. It is a further principal object of the invention for conducting the methods in electrochemical cells specially equipped with membranes, such as stable cation exchange types, stable anion exchange types, stable bipolar membranes, including multi-compartment cells, particularly three compartment electrochemical cells. It is yet a further object to conduct the methods of the invention by the steps of modifying electrolytes through incorporation of additives, e. It is still a further object of the invention to provide for methods of conducting paired electrochemical reactions in which a formaldehyde-containing catholyte is reduced to ethylene glycol while higher valence state oxidizing ions of a regeneratable redox reagent from the anolyte are reacted indirectly with oxidizable aromatic compounds to form secondary products, and particularly compounds which are oxidizable to polybasic acids, such as terephthalic acid. This includes methods for preparation of useful tertiary products like polyesters in reactions, according to the steps of: The present invention also contemplates paired electrochemical synthesis reactions in which ethylene glycol is prepared and other products, such as aldehydes, quinones, glycol esters, ethers, dioxolanes, and the like, are indirectly prepared at the anode. A process made compatible through this invention takes place simultaneously at the anode by reacting indirectly, anodically generated oxidizing products with an organic substrate to form secondary products. For purposes of this invention the expression "secondary product" is intended to mean any organic substance formed indirectly by reaction with oxidant produced at the anode which is not used in the synthesis of ethylene glycol at the cathode, and where appropriate can be reacted with the ethylene glycol prepared at the cathode to form useful tertiary products. Thus, one principal aspect of the invention relates to an electrochemical process in which ethylene glycol is synthesized at the cathode while a second reaction is also taking place at the anode, but significantly without consequential trade-offs in the ethylene glycol current efficiency at the cathode and without substantial losses of redox ions from the anolyte compartment, proton imbalance, etc. That is, by oxidizing at the anode concurrently, the lower valence state ions of a regeneratable

redox reagent to their higher valence oxidizing state and chemically reacting indirectly with an organic substrate, e. Such useful secondary products can be marketed as is through ordinary channels of commerce, but more preferably, polybasic acids are condensed with the ethylene glycol produced from the catholyte to prepare important tertiary products, like polyesters as part of the same process. Accordingly, the paired electrochemical synthesis processes of the present invention contemplate both electrochemical and chemical steps in the preparation of valuable secondary products as well as tertiary products formed when reacted with ethylene glycol made from the catholyte. In carrying out the objectives of this invention an electrochemical cell is provided with a suitable cathode, an anode and at least one ion-exchange membrane per unit cell to separate aqueous anolyte and catholyte solutions. Both the anolyte and catholyte preferably operate at about the same temperature. The catholyte comprises formaldehyde, supporting electrolyte salts, such as sodium formate, potassium acetate, sodium methanesulfonate, sodium chloride, etc. The ethylene glycol process is conducted at a current efficiency of at least 70 percent, and more preferably, maintained at current efficiencies in the range of 75 to 99 percent. To maintain the current efficiency at a high level, stable miscible or immiscible organic cosolvents can be added to the aqueous catholyte. Representative examples include sulfolane, tetra-hydrofuran, cyclohexane, ethyl acetate, acetonitrile and adiponitrile. Alcohol cosolvents should be avoided, particularly at concentrations greater than 0. Immiscible organic cosolvents of high extraction capability for ethylene glycol, like ethyl acetate and amyl acetate are especially useful in avoiding distillation of the aqueous electrolyte. Other cosolvents, such as sulfolane and adiponitrile are higher boiling and enable distillation of the glycol from the electrolyte-cosolvent mixture. The aqueous anolyte comprises as a principle component at least one regeneratable redox reagent having higher and lower valence state metal ions. For optimum efficient regeneration of the lower valence state ions of the regeneratable redox reagent to the higher valence oxidizing state and subsequent facile reaction with the organic substrate, either in the cell or preferably in a reaction zone outside the cell an oxidant regeneration catalyst may be added to the anolyte. The aqueous anolyte can also comprise stable organic cosolvents which can aid in solvating the aromatic organic substrates previously mentioned in synthesizing secondary products. The cosolvent may be miscible or immiscible with the aqueous phase, and depending largely on inertness to oxidation by the oxidant, may include such representative examples as sulfolane, ketones such as methyl ethyl ketone and dipropyl ketone, hydrocarbons like cyclohexane, nitriles like acetonitrile, propionitrile, adiponitrile and benzonitrile, ethers such as tetrahydrofuran and dioxane, organic carbonates such as propylene carbonate, esters like ethyl and propyl acetate, halocarbons like methylene chloride, chloroform, dichloroethane, trichloroethane and perfluoro-octane. Optionally, anionic and cationic surfactants or phase transfer reagents, such as sodium dodecylbenzene sulfonate and tetrabutylammonium hydroxide, respectively, may be added to the anolyte for some degree of emulsification with insoluble organic substrates, thereby facilitating reaction of the higher valence oxidizing ion therewith. In order to avoid cross-contamination of the anolyte and catholyte solutions ion-exchange membranes are a necessary component of the invention. Membranes perform as separators aiding in preventing losses of formaldehyde and ethylene glycol into the anolyte stream, and hence possible destruction of the formaldehyde and ethylene glycol, as well as the loss of valuable regeneratable redox reagent, both reduced and oxidized forms, into the catholyte where deleterious processes, such as cathode poisoning and membrane fouling can occur. Accordingly, membranes must be judiciously selected to be chemically, mechanically and thermally stable to these electrolytes while preventing the loss and destruction of reactant and product contained therein. Membranes are also chosen on the basis of cost, lowest cell voltage contribution and for their ionic selectivity, and may be either anionic, cationic or bipolar. Stable cation exchange membranes are generally preferred, especially for highly oxidizing acidic anolyte solutions. Of particular importance are the more oxidation stable fluorinated and perfluorinated type membranes which have higher temperature stability and resist thermal degradation in the temperature region of operation. Others are available from Asahi Glass and Tosoh. Because of their stability the perfluoro-sulfonic acid type cation exchange membranes are especially preferred with more powerful oxidants over a wide pH range and at higher operating temperatures. They, like other cation exchange type membranes exclude negatively charged redox species e.  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ , from crossing into the catholyte with consequent contamination of that

solution. Notwithstanding the generally favorable performance of these membranes, even with their judicious selection, they may still not be sufficient to overcome the separation problems associated with the paired electrochemical synthesis reactions with the simultaneous production of ethylene glycol according to the invention. In this regard, a principal problem associated with the use of cation exchange membranes is that they allow the positively charged metal ions of the regeneratable redox reagent in the anolyte compartment to pass through to the catholyte compartment in competition to the preferred process of proton transfer. Consequently, even with use of the preferred cation exchange membranes a pH imbalance occurs on the cathode side of the cell resulting in lower product output. With the use of such membranes costly losses of redox reagents in the catholyte stream can occur which means higher operating costs for recovery or replacement of these salts. In addition, redox ion buildup in the catholyte will eventually poison the cathode process. Accordingly, it was discovered that the foregoing problem can be overcome by maintaining the proton concentration in the anolyte compartment at as high a value as possible compared to the concentration of positively charged regeneratable redox species such that the protons needed for conducting the cathode reaction transfer through the cation exchange membrane to the catholyte compartment in preference to these metal ions. To achieve this result the present invention contemplates the addition to the anolyte compartment of a "strong acid" as the source of protons, the acid being added in an amount which is sufficient to inhibit passage of the metal ion regeneratable redox reagent from the anolyte to the catholyte. For purposes of this invention the expression --strong acid-- is intended to mean acids which when dissolved in water are virtually completely dissociated into ions see Quantitative Chemical Analysis, 4th. Representative strong acids include sulfuric, phosphoric, nitric, perchloric, as well as methanesulfonic and trifluoromethanesulfonic acids. The pH of the anolyte having the strong acid solution is generally less than about 2, and more preferably less than a pH of 1. While maintaining a high proton concentration in the anolyte relative to the positively charged redox species is an effective means for controlling losses of valuable metal ions to the catholyte stream with a cation exchange membrane, any losses in ethylene glycol current efficiency which might otherwise occur in the process gradually after a period of time can be further limited through use of metal ion complexing agents in the catholyte. This would include any of the well known complexing agents, such as ethylenediamine tetraacetic acid EDTA and nitrilotriacetic acid NTA to name but a few. Other means for recovering the metal ions from the catholyte would include precipitation, use of ion exchange resin beds, etc. While anion exchange membranes would appear to be useful in the paired electrochemical synthesis process, particularly since both the positively charged and negatively charged redox ion species as well as protons are unable to readily transfer through the positively charged membrane from the anolyte to the catholyte compartment, anion exchange membranes like the preferred cation exchange type cannot be utilized in the paired process without experiencing significant operating problems. In this regard, anionic species present in the catholyte are able to transfer through the membrane to the anolyte. It was found that anions like formate, acetate and chloride used in the catholyte as supporting electrolytes in the electroreduction of formaldehyde are readily oxidized at the anode or by electrogenerated oxidant. Furthermore, the pH of the catholyte progressively becomes more alkaline as electrolysis proceeds requiring the continuous addition of acid. Similarly, the anolyte becomes more acidic because of protons generated in the anolyte stream as the oxidant is formed.

**Chapter 6 : Acyl group: Definition with Acyl group Pictures and Photos**

*Book digitized by Google from the library of Harvard University and uploaded to the Internet Archive by user tpb.*

Mesitylene or 1,3,5-trimethylbenzene is a derivative of benzene with three methyl substituents positioned symmetrically around the ring. The other two isomeric trimethylbenzenes are 1,2,4-trimethylbenzene pseudocumene and 1,2,3-trimethylbenzene hemimellitene. Mesitylene is a colourless liquid with sweet aromatic odor. It is a component of coal tar, which is its traditional source. It is a precursor to diverse fine chemicals. The mesityl group Mes is a substituent with the formula  $\text{CHMe}_2$  and is found in various other compounds. Using manganese dioxide, a milder oxidising agent, 3,5-dimethyl benzaldehyde is formed. Mesitylene is oxidised by trifluoroacetic acid to produce mesitol 2,4,6-trimethylphenol. This derivative is prepared by selective mononitration of mesitylene, avoiding oxidation of the methyl groups. In the electronics industry, mesitylene has been used as a developer for photopatternable silicones due to its solvent properties. The three aromatic hydrogen atoms of mesitylene are in identical chemical shift environments. Therefore, they only give a single peak near  $\delta$  6. For this reason, mesitylene is sometimes used as an internal standard in NMR samples that contain aromatic protons. The correct empirical formula was provided by August W. Due to its large steric demand, the mesityl group is used as a large blocking group in asymmetric catalysis to enhance diastereo- or enantioselectivity and organometallic chemistry to stabilize low oxidation state or low coordination number metal centers. Safety and the environment Mesitylene is also a major urban volatile organic compound VOC which results from combustion. It plays a significant role in aerosol and tropospheric ozone formation as well as other reactions in atmospheric chemistry. Zhao, Jun; Zhang, Renyi Systematic organic chemistry 3E. Fluorine in Organic Chemistry. Mill Valley, CA,

**Chapter 7 : USA - Oxidation of alkylbenzene carboxylic acids - Google Patents**

*The Polybasic Acids of Mesitylene by Mary Bidwell Breed () "A more remarkable example of this is that although only one acyl group can be introduced into benzene.*

Simultaneously, a compatible process is also conducted at the anode of the same electrochemical cell by reacting indirectly generated anode products with organic substrates to form secondary products, such as polybasic acids. The process is especially advantageous in that such secondary products, where appropriate can be further reacted with the ethylene glycol prepared from the catholyte of the same cell to form useful tertiary products, especially polyesters like polyethylene terephthalate. Mole ratios of ethylene glycol and polybasic acid can be controlled through selective use of regeneratable redox reactant. Description BACKGROUND OF THE INVENTION The present invention relates generally to methods of conducting paired synthesis reactions electrochemically, and more specifically, to the preparation of ethylene glycol at the cathode of an electrochemical cell while simultaneously producing a regeneratable redox reagent at the anode of the same cell, which redox reagent can be reacted with an organic substrate to prepare a secondary product indirectly. Ethylene glycol is a major industrial chemical with worldwide production of about 20 billion pounds per year. Ethylene glycol is widely used in manufacturing polyester films and fibers and as an automotive coolant and antifreeze. The major source of ethylene glycol is from epoxidation of ethylene which is derived from petroleum, followed by hydration to form the glycol. However, dwindling petroleum reserves and petroleum feedstocks coupled with escalating prices has led to development of alternative routes based on syngas. Representative processes are described in U. In a recent patent to N. Significant effort has been made to improve the economics for the electrochemical synthesis of ethylene glycol. One such example is found in U. That is, the U. Accordingly, the present invention contemplates even more economically attractive electrochemical synthesis reactions with the simultaneous production of ethylene glycol wherein two or more useful products are generated simultaneously at the anode and cathode of the same electrochemical cell, and where the anode products are formed indirectly, hereinafter referred to as "paired electrochemical synthesis". The process is specially significant in light of the paired products ability to share in capital costs for cells, as well as operating costs, and particularly power. But, the process is also quite surprising in view of the fact that usually paired reactions cannot be conducted successfully side-by-side in the same electrochemical cell due to fundamental incompatibilities in cathodic and anodic reactions, e. In the absence of sufficient protons a pH imbalance occurs on the cathode side. This will depress the conversion efficiency of formaldehyde to ethylene glycol which translates into greater power consumption and costs per unit of product produced. In addition, passage of these metal ions of regeneratable redox reagents from the anode to the cathode side, has a tendency to inhibit the electroreduction of formaldehyde to ethylene glycol by "poisoning" the carbon cathode. Consequently, the hydrogen current efficiency increases and the desired ethylene glycol current efficiency of at least 70 percent decreases. Membranes are also subject to destruction by oxidants formed in the anolyte. Moreover, back-transfer of catholyte species, particularly organics, such as formaldehyde, ethylene glycol and oxidizable electrolyte anions, such as formate, into the anolyte causes deactivation of oxidant species and current efficiency losses. Accordingly, the present invention provides for important technical improvements in the electrochemical production of ethylene glycol making this method even more economic through a paired reaction format. It is a further principal object of the invention for conducting the methods in electrochemical cells specially equipped with membranes, such as stable cation exchange types, stable anion exchange types, stable bipolar membranes, including multi-compartment cells, particularly three compartment electrochemical cells. It is yet a further object to conduct the methods of the invention by the steps of modifying electrolytes through incorporation of additives, e. It is still a further object of the invention to provide for methods of conducting paired electrochemical reactions in which a formaldehyde-containing catholyte is reduced to ethylene glycol while higher valence state oxidizing ions of a regeneratable redox reagent from the anolyte are reacted indirectly with oxidizable aromatic compounds to form secondary products, and particularly compounds which are oxidizable to polybasic acids, such as terephthalic acid. This includes methods for

preparation of useful tertiary products like polyesters in reactions, according to the steps of: The present invention also contemplates paired electrochemical synthesis reactions in which ethylene glycol is prepared and other products, such as aldehydes, quinones, glycol esters, ethers, dioxolanes, and the like, are indirectly prepared at the anode. A process made compatible through this invention takes place simultaneously at the anode by reacting indirectly, anodically generated oxidizing products with an organic substrate to form secondary products. For purposes of this invention the expression "secondary product" is intended to mean any organic substance formed indirectly by reaction with oxidant produced at the anode which is not used in the synthesis of ethylene glycol at the cathode, and where appropriate can be reacted with the ethylene glycol prepared at the cathode to form useful tertiary products. Thus, one principal aspect of the invention relates to an electrochemical process in which ethylene glycol is synthesized at the cathode while a second reaction is also taking place at the anode, but significantly without consequential trade-offs in the ethylene glycol current efficiency at the cathode and without substantial losses of redox ions from the anolyte compartment, proton imbalance, etc. That is, by oxidizing at the anode concurrently, the lower valence state ions of a regeneratable redox reagent to their higher valence oxidizing state and chemically reacting indirectly with an organic substrate, e. Such useful secondary products can be marketed as is through ordinary channels of commerce, but more preferably, polybasic acids are condensed with the ethylene glycol produced from the catholyte to prepare important tertiary products, like polyesters as part of the same process. Accordingly, the paired electrochemical synthesis processes of the present invention contemplate both electrochemical and chemical steps in the preparation of valuable secondary products as well as tertiary products formed when reacted with ethylene glycol made from the catholyte. In carrying out the objectives of this invention an electrochemical cell is provided with a suitable cathode, an anode and at least one ion-exchange membrane per unit cell to separate aqueous anolyte and catholyte solutions. Both the anolyte and catholyte preferably operate at about the same temperature. The catholyte comprises formaldehyde, supporting electrolyte salts, such as sodium formate, potassium acetate, sodium methanesulfonate, sodium chloride, etc. The ethylene glycol process is conducted at a current efficiency of at least 70 percent, and more preferably, maintained at current efficiencies in the range of 75 to 99 percent. To maintain the current efficiency at a high level, stable miscible or immiscible organic cosolvents can be added to the aqueous catholyte. Representative examples include sulfolane, tetra-hydrofuran, cyclohexane, ethyl acetate, acetonitrile and adiponitrile. Alcohol cosolvents should be avoided, particularly at concentrations greater than 0. Immiscible organic cosolvents of high extraction capability for ethylene glycol, like ethyl acetate and amyl acetate are especially useful in avoiding distillation of the aqueous electrolyte. Other cosolvents, such as sulfolane and adiponitrile are higher boiling and enable distillation of the glycol from the electrolyte-cosolvent mixture. The aqueous anolyte comprises as a principle component at least one regeneratable redox reagent having higher and lower valence state metal ions. For optimum efficient regeneration of the lower valence state ions of the regeneratable redox reagent to the higher valence oxidizing state and subsequent facile reaction with the organic substrate, either in the cell or preferably in a reaction zone outside the cell an oxidant regeneration catalyst may be added to the anolyte. The aqueous anolyte can also comprise stable organic cosolvents which can aid in solvating the aromatic organic substrates previously mentioned in synthesizing secondary products. The cosolvent may be miscible or immiscible with the aqueous phase, and depending largely on inertness to oxidation by the oxidant, may include such representative examples as sulfolane, ketones such as methyl ethyl ketone and dipropyl ketone, hydrocarbons like cyclohexane, nitriles like acetonitrile, propionitrile, adiponitrile and benzonitrile, ethers such as tetrahydrofuran and dioxane, organic carbonates such as propylene carbonate, esters like ethyl and propyl acetate, halocarbons like methylene chloride, chloroform, dichloroethane, trichloroethane and perfluoro-octane. Optionally, anionic and cationic surfactants or phase transfer reagents, such as sodium dodecylbenzene sulfonate and tetrabutylammonium hydroxide, respectively, may be added to the anolyte for some degree of emulsification with insoluble organic substrates, thereby facilitating reaction of the higher valence oxidizing ion therewith. In order to avoid cross-contamination of the anolyte and catholyte solutions ion-exchange membranes are a necessary component of the invention. Membranes perform as separators aiding in preventing losses of formaldehyde and ethylene glycol into the anolyte stream, and hence possible

destruction of the formaldehyde and ethylene glycol, as well as the loss of valuable regeneratable redox reagent, both reduced and oxidized forms, into the catholyte where deleterious processes, such as cathode poisoning and membrane fouling can occur. Accordingly, membranes must be judiciously selected to be chemically, mechanically and thermally stable to these electrolytes while preventing the loss and destruction of reactant and product contained therein. Membranes are also chosen on the basis of cost, lowest cell voltage contribution and for their ionic selectivity, and may be either anionic, cationic or bipolar. Stable cation exchange membranes are generally preferred, especially for highly oxidizing acidic anolyte solutions. Of particular importance are the more oxidation stable fluorinated and perfluorinated type membranes which have higher temperature stability and resist thermal degradation in the temperature region of operation. Others are available from Asahi Glass and Tosoh. Because of their stability the perfluoro-sulfonic acid type cation exchange membranes are especially preferred with more powerful oxidants over a wide pH range and at higher operating temperatures. They, like other cation exchange type membranes exclude negatively charged redox species e.  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{FeCN}_6^{4-}$ , from crossing into the catholyte with consequent contamination of that solution. Notwithstanding the generally favorable performance of these membranes, even with their judicious selection, they may still not be sufficient to overcome the separation problems associated with the paired electrochemical synthesis reactions with the simultaneous production of ethylene glycol according to the invention. In this regard, a principal problem associated with the use of cation exchange membranes is that they allow the positively charged metal ions of the regeneratable redox reagent in the anolyte compartment to pass through to the catholyte compartment in competition to the preferred process of proton transfer. Consequently, even with use of the preferred cation exchange membranes a pH imbalance occurs on the cathode side of the cell resulting in lower product output. With the use of such membranes costly losses of redox reagents in the catholyte stream can occur which means higher operating costs for recovery or replacement of these salts. In addition, redox ion buildup in the catholyte will eventually poison the cathode process. Accordingly, it was discovered that the foregoing problem can be overcome by maintaining the proton concentration in the anolyte compartment at as high a value as possible compared to the concentration of positively charged regeneratable redox species such that the protons needed for conducting the cathode reaction transfer through the cation exchange membrane to the catholyte compartment in preference to these metal ions. To achieve this result the present invention contemplates the addition to the anolyte compartment of a "strong acid" as the source of protons, the acid being added in an amount which is sufficient to inhibit passage of the metal ion regeneratable redox reagent from the anolyte to the catholyte. For purposes of this invention the expression --strong acid-- is intended to mean acids which when dissolved in water are virtually completely dissociated into ions see Quantitative Chemical Analysis, 4th. Representative strong acids include sulfuric, phosphoric, nitric, perchloric, as well as methanesulfonic and trifluoromethanesulfonic acids. The pH of the anolyte having the strong acid solution is generally less than about 2, and more preferably less than a pH of 1. While maintaining a high proton concentration in the anolyte relative to the positively charged redox species is an effective means for controlling losses of valuable metal ions to the catholyte stream with a cation exchange membrane, any losses in ethylene glycol current efficiency which might otherwise occur in the process gradually after a period of time can be further limited through use of metal ion complexing agents in the catholyte. This would include any of the well known complexing agents, such as ethylenediamine tetraacetic acid EDTA and nitrilotriacetic acid NTA to name but a few. Other means for recovering the metal ions from the catholyte would include precipitation, use of ion exchange resin beds, etc. While anion exchange membranes would appear to be useful in the paired electrochemical synthesis process, particularly since both the positively charged and negatively charged redox ion species as well as protons are unable to readily transfer through the positively charged membrane from the anolyte to the catholyte compartment, anion exchange membranes like the preferred cation exchange type cannot be utilized in the paired process without experiencing significant operating problems. In this regard, anionic species present in the catholyte are able to transfer through the membrane to the anolyte. It was found that anions like formate, acetate and chloride used in the catholyte as supporting electrolytes in the electroreduction of formaldehyde are readily oxidized at the anode or by electrogenerated oxidant. Furthermore, the pH of the catholyte progressively becomes more

alkaline as electrolysis proceeds requiring the continuous addition of acid. Similarly, the anolyte becomes more acidic because of protons generated in the anolyte stream as the oxidant is formed. The anion portion of the acid passes through the membrane from the catholyte to the anolyte compartment. Accordingly, it was discovered that the foregoing problems associated with the use of anion exchange membranes can be overcome through use in the catholyte of the salt of an acid with an oxidation stable anion. Sufficient oxidation stable acid is added to the catholyte to maintain the pH of the catholyte in the range from about 5 to about 8. Representative examples of useful acids include those in which the anion of the acid is either sulfate, bisulfate, phosphate, methanesulfonate, trifluoromethanesulfonate, fluoride, tetrafluoroborate or hexafluorophosphate. The special advantage of employing an oxidation stable acid is that since the acid added to the catholyte and the anolyte will be the same. The recovered acid can then be recycled back to the catholyte compartment for purposes of maintaining the pH range optimal for the cathode compartment. A further alternative to cation and anion exchange membranes previously described, are bipolar type membranes. Although less preferred because of higher capital costs and potentially higher operating costs due to greater IR drop, bipolar membranes nevertheless are advantageous because they have dual polarity, i. They essentially "split" water allowing protons to transfer to the catholyte from the cationic side and hydroxide ions to transfer to the anolyte from the anionic side without permitting metal redox ion species from penetrating into the catholyte. Thus, stable bipolar membranes, and particularly fluorinated bipolar types, such as those manufactured by Tosoh are practical in solving the problems previously described in connection with selective transmission of ions in the paired electrochemical synthesis methods disclosed herein. The electrochemical cells of the present invention are usually two compartment cells having anolyte and catholyte compartments. Such cells may be batch or continuous flow types, as well as monopolar and bipolar in design which may include plate and frame types, packed bed electrodes, fluidized bed electrodes, other high area three dimensional electrodes, as well as capillary gap and zero gap designs, etc. Although such two compartment membrane divided cells are preferred, the problems previously described in connection with the transmission of various organic and ionic species between compartments of the cells can also be remedied by means of membrane divided three compartment type cells of known design. This alternative embodiment contemplates a central or buffer compartment situated between anolyte and catholyte compartments. The central compartment may be filled with an aqueous strong acid electrolyte and be bounded by two stable cation exchange membranes, two anion exchange membranes, or a cation and an anion exchange membrane, preferably fluorinated if the anion exchange membrane separates the anolyte and the central compartment electrolyte. Preferably, with a three compartment cell at least one membrane is a stable fluorinated anion exchange type. A three compartment electrochemical cell is desirable because it minimizes losses of regeneratable redox reagent ions into the catholyte compartment. Instead, in the case of two cation exchange membranes as an example, any redox metal ions passing through the membrane on the anolyte side of the cell accumulate in the acidic central compartment while protons from the anolyte compartment are able to preferentially pass to the catholyte compartment. Those metal ions in the central compartment may be continuously removed by methods generally known in the art, such as ion-exchange resins or electro-dialysis, and subsequently recovered for recycling back to the anolyte stream. Secondary products are prepared by electrochemically oxidizing the lower valence state ions of the regeneratable redox reagent at the anode to the higher valence oxidizing state while simultaneously forming ethylene glycol at the cathode of the same electrochemical cell without trade-offs in current efficiencies, i. In this case, it is preferable to transfer the anolyte comprising the higher valence oxidizing ions to a separate reaction vessel where it is contacted with the organic substrate feed under agitation. The organic substrate may be introduced into the reaction vessel as a pure substrate, dissolved or dispersed in the aqueous phase of the anolyte, or dissolved in a cosolvent with the aqueous solution. The reaction products, spent oxidant and secondary product may be separated by precipitation of the product, or by phase-separation, extraction, electrolysis, distillation, etc.

## DOWNLOAD PDF POLYBASIC ACIDS OF MESITYLENE.

*In the case of mesitylene, it has been found that even a third group can be introduced by sufficiently energetic means. E. Louise succeeded in getting successively one, two and three benzoyl groups into mesitylene, the latter by using a large excess of benzoyl chloride and heating to for several hours.*