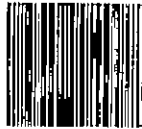


PETITORIO


Industria y Comercio
 SUPERINTENDENCIA



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 Trámite: 002 PATENTES D 1 REGISTRO/ 411 PRESENTAC
 Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

FORMULARIO UNICO DE SOLICITUD DE PATENTE 2000-3

1 SOLICITUD DE:			
☒ Patente de Invención ☐ Patente de Modelo de Utilidad			
2 SOLICITANTE (71)	Nombre: ATOFINA CHEMICALS, INC. sociedad constituida y existente bajo las leyes del Estado de Pennsylvania, Estados Unidos de América Dirección: 2000 Market Street, Philadelphia, Pennsylvania 19103-3222, Estados Unidos de América Teléfono: 546 09 70 E-mail: clientes@camyp.com Fax: 249 40 70 Domicilio: Philadelphia, Pennsylvania, Estados Unidos de América		IDENTIFICACION C.C. ☐ NIT ☐ C.E. ☐ Otro ☐ Número:
3 REPRESENTANTE O APODERADO (74)	Nombre: Emilio Ferrero Dirección: Carrera 4ª No. 72-35 Teléfono: 347 36 11 E-mail: cavelier@cavelier.com Fax: 217 92 11 Domicilio: Bogotá, Colombia		IDENTIFICACION C.C. ☒ NIT ☐ C.E. ☐ Otro ☐ Número: 438.019 TP 31.929
4 INVENTOR(ES) (72)	Nombre: Conor Michael DOWLING Dirección: 1657 Sullivan Drive, Blue Bell, Pennsylvania 19422, Estados Unidos de América Nombre: Bin CHEN Dirección: 1197 Heyward Road, Wayne, Pennsylvania 19087, Estados Unidos de América Nombre: Sri Ram SESHADRI Dirección: 46 Paddock Way, Holland, Pennsylvania 18966, Estados Unidos de América		IDENTIFICACION C.C. ☐ NIT ☐ C.E. ☐ Otro ☐ Número:
5 TITULO (54) POLICONDENSACIÓN DE POLIÉSTERES CON CATALIZADOR Y MEJORADOR DE CATALIZADOR			
6 Clasificación Internacional (51) C08G 03/82; B01J31/04			
7 Prioridad SI ☒ NO ☐	(33) País de Origen US	(32) Fecha 29 de Junio de 2001	(31) Número de Solicitud 09/895,990
8 Para publicar a partir de la fecha de la presente solicitud a los 6 meses ☐ 12 meses ☐ 18 meses ☒ Otro ☐			

9

Comprobante de pago No. 01-77,143 por valor de \$356,640 Fecha 10 de diciembre de 2001
 Comprobante de pago No. 02-405 por valor de \$ 21,360 Fecha 8 de enero de 2002
 Comprobante de pago No. 01-77,111 por valor de \$100.000 Fecha 10 de diciembre de 2001
 Comprobante de pago No. 02-350 por valor de \$ 6.000 Fecha 8 de enero de 2002

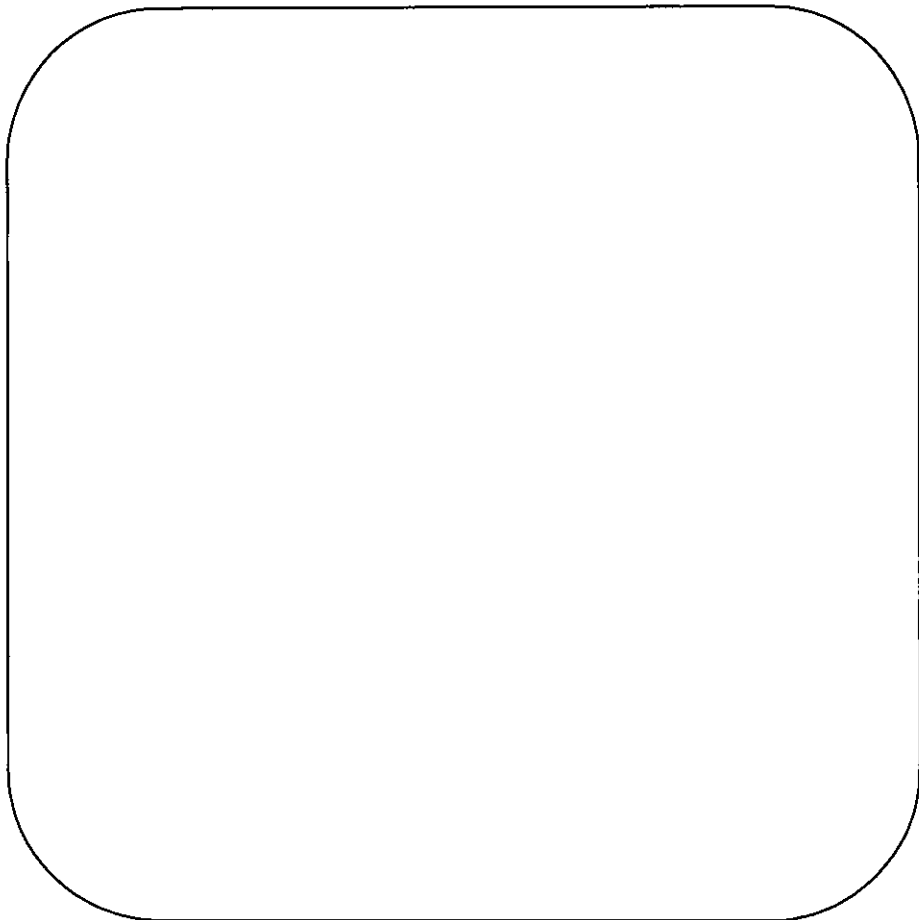
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ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Comprobante de pago de la tasa por concepto de excedente de palabras en la publicación
- ☒ Comprobante de pago por reivindicación de prioridad
- ☒ Certificado de existencia y representación legal cuando el solicitante sea persona jurídica
- ☒ Poderes, si fuere el caso
- ☐ Copia certificada de la primera solicitud, si se reivindica prioridad
- ☐ Traducción simple de la primera solicitud, si se reivindica prioridad
- ☐ Documento de cesión del inventor al solicitante o a su causante
- ☒ Descripción de la invención *(En Inglés)*
- ☒ Una o más reivindicaciones *(En Inglés)*
- ☐ Dibujos y/o planos necesarios
- ☐ De ser el caso, copia del contrato de acceso
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas
- ☐ De ser el caso, certificado de depósito del material biológico
- ☐ Arte final 12 x 12.

11

FIGURA CARACTERISTICA:



12

NOMBRE: EMILIO FERRERO

FIRMA:

C.C. 438.019 de Usaquén T.P. 31.929

Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página

2

POLYESTER POLYCONDENSATION WITH CATALYST AND A CATALYST ENHANCER

IR 3480A CIP

Reference to Related Application

[0001] This application is a continuation-in-part of United States Patent Application Serial Number 09/747,115, filed December 22, 2000, which claims priority of U.S. Provisional Application No. 60/175,006, filed January 7, 2000, which disclosures are incorporated herein by reference.

Background of the Invention

[0002] This invention relates to synergistic combinations of titanium containing catalysts and catalyst enhancers of carboxylic acid or oxalic acid or their Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and ammonium salts that are useful for manufacturing polyesters. The synergistic combination of the titanium containing catalysts with a catalyst enhancer such as an oxalic acid, an oxalic acid salt or a carboxylic acid or a carboxylic acid salt provides fast reactions with improved properties such as reduced acetaldehyde content and good color properties for the resulting polyester at substantially reduced catalyst levels.

Description of the Prior Art

[0003] Polycondensation reactions that produce polyesters require an extremely long period of time that is significantly reduced by a suitable catalyst. Various types of catalysts are used to shorten the reaction time. For example, antimony trioxide, antimony triacetate and antimony trisglycoxide are generally used as polycondensation catalysts.

[0004] Titanyl oxalate compounds have been suggested as catalysts for polycondensation reactions to produce polyesters. However, titanyl oxalate catalysts when used as polycondensation catalysts for polyesters have caused color problems in the resulting polyester.

[0005] Polyesters are obtained by esterification, ester interchange or polycondensation of dibasic acids such as terephthalic acid and isophthalic acid or esters

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thereof, functional derivatives of acid chlorides and glycols such as ethylene glycol and tetramethylene glycol or oxides thereof and functional derivatives of carbonic acid derivatives. In this case, a single polyester is obtained when one dibasic acid component and glycol component are used. Mixed copolyesters can be obtained when at least two or more types of dibasic acid component and glycol component are mixed, esterified or subjected to ester interchange and then subjected to polycondensation. When a single polyester or two or more initial polycondensates of a mixed copolyester are subjected to polycondensation, an ordered polyester is obtained. In this invention, the term polyester is a general designation for these three types.

[0006] Prior literature has disclosed titanyl oxalate compounds for use as polycondensation catalysts for polyesters. The titanyl oxalate compounds disclosed include potassium titanyl oxalate, ammonium titanyl oxalate, lithium titanyl oxalate, sodium titanyl oxalate, calcium titanyl oxalate, strontium titanyl oxalate, barium titanyl oxalate, zinc titanyl oxalate and lead titanyl titanate. However, based upon the examples in such literature references, only potassium and ammonium titanyl oxalate have actually been used to catalyze the polyester forming reaction. See for example Japanese Patent Publication 42-13030, published on 25, July, 1967. European Patent application EP 0699700 A2 published 3/6/1996 assigned to Hoechst and entitled "Process for production of Thermostable, Color-neutral, Antimony-Free Polyester and Products Manufactured From It" discloses the use as polycondensation catalyst, however only potassium titanyl oxalate and titanium isopropylate were used for such a catalyst, and, while improved color and antimony free polyester are disclosed, cobalt or optical brighteners were also employed. Other patents have disclosed potassium titanyl oxalate as a polycondensation catalyst for making polyester such as U.S. Patent 4,245,086, inventor Keiichi Uno et al., Japanese Patent JP 06128464, Inventor Ishida, M. et al. U. S. Patent 3,951,886, entitled "Process of Producing Polyester Resin" of Hideo, M. et al, at column 3, line 59 to column 4, line 10, contains a disclosure of titanyl oxalate catalysts for polyesters including a listing of many types of titanyl oxalate catalyst. However, only potassium titanyl oxalate and ammonium titanyl oxalate were used in the examples and lithium titanyl oxalate was not even listed among their preferred titanyl oxalate catalysts.

[0007] Titanium based catalysts have shown very high polycondensation activity, however; the resulted polyesters are yellowish color which will limit their applications. Therefore, prior art activity has been directed towards the development of modified titanium catalysts. Titanium compounds are not a good sole catalyst. Ti requires a cocatalysts or modifiers/promoters to form composite catalyst. Titanium compounds in the general formula of $Ti(OR)_4$, $Ti^{(III)}Ti^{(IV)}O_{(3+y)/2}$, $RO[Ti(OR)_2O]_nR$ have been widely claimed by others. Cocatalysts or modifiers/promoters, such as antimony compounds, tin compounds, zirconium compounds, silicon compounds, cobalt compound, aluminum compounds, alkali metal compounds, rare earth metal compounds, magnesium compounds, germanium compounds, zinc compounds, lanthanide series compounds, phosphorus compounds, halides, sulfur containing compounds, ammonia hydroxide, and amines, have been claimed together with Ti compounds.

[0008] US patent 6,166, 170, E.I. du Pont de Nemours and Company, issued on 12/26/2000 discloses a catalyst composition of a titanium compound, a complexing agent, and an aqueous solution of hypophosphorous acid or a salt. The titanium compound has a general formula, $Ti(OR)_4$, combined with a zirconium compound, $Zr(OR)_4$. The complex agents are hydroxycarboxylic acids, alkanolamines, aminocarboxylic acids and their combinations of two or more.

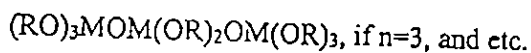
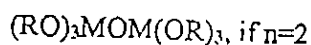
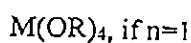
[0009] US patent 6,066,714, E.I. du Pont de Nemours and Company, issued on 5/23/2000, discloses an organic titanium compound, a phosphorus compound, an amine, and a solvent as a catalyst. The organic compound is $Ti(OR)_4$. The phosphorus compound is either $(RO)_x(PO)(OH)_{3-x}$ or $(RO)_x(P_2O_3)(OH)_{4-y}$. The amine is a tertiary amine. Aluminum, cobalt, antimony compounds and their combination were claimed as cocatalysts.

[00010] US patent 6,034,203, E.I. du Pont de Nemours and Company, issued on 3/7/2000, discloses a catalytic process that can be used in oligomerization, polymerization, or depolymerization. The catalyst has the formula of $M_xTi^{(III)}Ti^{(IV)}O_{(x+3-y)/2}$, where M is an alkali metal, such as Li; x and y are numbers greater than or equal to zero wherein if x equals zero, y is a number less than $\frac{1}{2}$.

[00011] US 5,981,690, E.I. du Pont de Nemours and Company, issued on 11/9/1999. This patent shows a catalyst solution containing an organic titanate ligand, organic silicates

and/or zirconates, and phosphorus compounds. Titanium has a formula of $Ti(OR)_4$; silicon and zirconium compounds can be organic ortho silicate and zirconate; phosphorus compound can be an organic phosphonic or phosphinic acid. The solvent used was ethylene glycol. The catalyst was claimed to be used in fabrication of PET, PEI, PPT, PBT, and etc.

[00012] US 5,866, 710, Tioxide Specialties Limited, issued on 2/2/1999 (EP 0 812 818 A1, published on 12/17/1999). A process of preparing an ester is disclosed in the presence of a catalyst and a base, the product from orthoesters and condensed orthoesters of zirconium and titanium. The orthoesters have the formula of $M(OR)_4$; the condensed orthoesters, $RO[M(OR)_2O]_nR$; where M is either zirconium or titanium. This compound can be illustrated as the following,



The base can be selected sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, magnesium hydroxide and ammonia.

[00013] WO 00/71252 A1, ACMA Limited, published on 11/30/2000. An esterification catalyst composition was disclosed. The catalyst contains 1) hydrolysis product of orthoesters and condensed orthoesters of titanium, zirconium or aluminum; 2) an alcohol containing at least two hydroxyl groups; 3) an organophosphorus compound containing at least one P-OH group and a base; 4) a compound of germanium, antimony or tin.

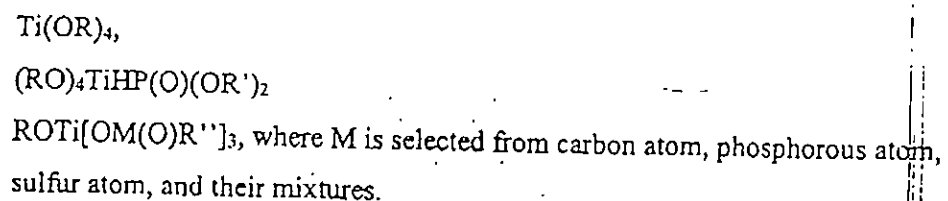
[00014] WO 99/28033 A1, Tioxide Specialties, published on 6/10/1999. An esterification catalyst composition was disclosed. The catalyst contains 1) hydrolysis product of orthoesters and condensed orthoesters of titanium, zirconium or aluminum; 2) an alcohol containing at least two hydroxyl groups; 3) an organophosphorus compound containing at least one P-OH group and a base.

[00015] WO 97/47675 A1, Imperial Chemical Industries PLC, published on 12/18/1997 also EP 0906356 jointly with E. I. Du Pont De Nemours & Company Inc. A catalyst is disclosed that is obtained by reacting an alkyl titanate or alkyl zirconate, an alcohol, a 2-hydroxy carboxylic acid and a base. A cobalt (II) salt, a phosphorus compound, and a sodium compound were claimed as catalyst components.

[00016] US patent 5,874,517, Hoechst Celanese Corporation, issued on 2/23/1999. An improved low acetaldehyde process was disclosed. The process utilized mixed Ti and Sb catalysts, however; potassium titanyl oxalate was suggested as a sole catalyst (col. 6, lines 21 and 22). Potassium titanyl oxalate as a polycondensation catalyst was claimed in claims 15 to 20.

[00017] US patent 5,902,873, General Electric Company, issued on 5/11/1999; (EP 0 909 774 A1, published on 4/21/1999. A catalyst composition for the preparation of a polyester on copolyester is disclosed. The catalyst was composed of 1) a titanium or zirconium based compound, general formula, $Ti(OR)_4$ or $Zr(OR)_4$, the titanium compounds were water-stable; 2) a lanthanide series compound, such as lanthanum, samarium, europium, erbium, terbium, and cerium; 3) a hafnium based compound; 4) a phosphate-forming compound, such as alkali metal phosphates, alkali metal phosphates, alkali hypophosphates, and alkali metal polyphosphates. The combination of the above components was claimed. In particular, titanium oxide acetylacetonate was claimed (in claim 3, col. 13, lines 52 and 53).

[00018] US patent 6,133,404, National Institute of Technology and Quality, issued on 10/17/2000. A polyester and formation process is disclosed in the presence of a composite catalyst that consists of a titanium compound, a zinc compound, an antimony compound, and a phosphorous compound. This catalyst improved the rate of polyester production and properties of the polymers, in particular, biodegradability of the polymer. The titanium compound has the following general formula,



[00019] The zinc compound can be zinc oxide, zinc acetate, zinc chloride, zinc hydroxide and their mixtures. An antimony compound can be selected from antimony chloride, antimony acetate, antimony oxide and their mixtures. A phosphorous compound can be one of the following, Phosphoric acid compounds, phosphite compounds, phosphonic acid compounds, phosphinic acid compound, and their mixtures.

[00020] US patent 5,714,570, Korea Institute of Science and Technology, issued on 2/3/1998. A method for the preparation of polyester by use of a composite catalyst was revealed. The composite catalyst consists of a compound of Sb, a compound of Ti, and a compound of Sn. A compound of Ti has a general formula of $(R_1O)_4TiHP(O)(OR_2)_2$, and Tin compound, $(R_3)_2SnX$, where X is selected from sulfur, oxygen, halogen, and a compound containing an ether, a thio or an ester bond. In particular, potassium titanium oxyoxalate was claimed as shown in claim 9 (col. 10, lines 52 and 53) other metals (such as germanium, zinc, manganese, alkali, and alkali earth) compounds were also claimed. It was disclosed that antioxidant, such as a hindered phenol, was used in the process.

[00021] US patent 6,143,837, Sinco Ricerche, S.P.A, issued on 11/7/2000. A process of preparation of polyester resin utilizing Ti compound catalyst was disclosed. The activity of Ti catalysts was shown to be four time higher than S21 catalyst. The titanium compounds can be selected from the group consisting of alkoxides of titanium, acetyl acetonates of titanium, dioxide of titanium, and titanium phosphites. Silica mixed with Ti was used in their examples (but not claimed). A cobalt compound was suggested to be used as a colorants.

Summary of the Invention

[00022] The present invention is based upon the discovery of a synergistic combination of a titanium containing catalyst and a catalyst enhancer. This invention provides a novel catalytic mixture comprising a titanium containing catalyst of the formula $X_mTiO(C_2O_4)_2(H_2O)_n$, where X is selected from the group consisting of H, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, and ammonium, $m=1$ or 2 ; and a catalyst enhancer comprising oxalic acid or carboxylic acid containing 1 to 26 carbon atoms or their corresponding Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, or ammonium salt. Also provided is a novel enhanced catalyst mixture comprising a titanium compound of the formula X_mTiY_o with X selected from the group consisting of: H, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and ammonium, $m=1$ or 2 , Y is a ligand of the formula $C_aH_bO_c$, $a=0$ to 30 , $b=0$ to 60 , and $c=1$ to 10 ; $o=2, 3, 4$, and a catalyst enhancer of an oxalic acid or its corresponding Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba or ammonium salt. An improved three component enhanced catalyst mixture can be obtained by the addition of second catalyst to either of the above enhanced catalyst

mixtures, the second catalyst being a compound containing antimony or germanium. Also provided are enhanced antimony containing catalysts comprising the mixture of an antimony containing catalyst and an enhancer of an oxalic acid or its corresponding Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba or ammonium salt.

[00023] This invention also provides an improved process of producing polyester by the polycondensation of polyester forming reactants in the presence of a catalytically effective amount of a polycondensation catalyst, wherein the improvement comprises utilizing, as the polycondensation catalyst, the synergistic combination of a titanium containing catalyst and the catalyst enhancer described in the preceding paragraph. A novel polyester is also provided containing the synergistic combination of a titanium containing catalyst and the catalyst enhancer described in the preceding paragraph. The improved process produces an improved polyester having lower acetaldehyde numbers and good color. The titanium containing catalyst and catalyst enhancer composition can be used as a polycondensation catalyst in combination with other catalysts to achieve synergistic catalytic activity.

Detailed Description of the Invention

[00024] The production of polyester by polycondensation of polyester forming reactants is well known to those skilled in the polyester art. A conventional catalyst for the reaction is antimony oxide. The present invention is based upon the discovery of a synergistic relationship between titanium containing catalysts and carboxylic or oxalate catalyst enhancers. The catalyst and catalyst enhancer is surprisingly superior in catalyst performance for polycondensation reactions by providing good catalyst activity at reduced catalyst loadings and superior brightness in the resulting polyester.

[00025] Reactants for forming polyesters via a polycondensation reaction are well known to those skilled in the art and disclosed in patents such as U.S. Patent 5,198,530, inventor Kyber, M., et al., U.S. Patent 4,238,593, inventor B. Dub, U.S. Patent 4,356,299, inventor Cholod et al, and U.S. Patent 3,907,754, inventor Tershasy et al, which disclosures are incorporated herein by reference. The art is also described in "Comprehensive Polymer Science, Ed. G.C. Eastmond, et al, Pergamon Press, Oxford 1989, vol. 5, pp. 275-315, and by R.E. Wilfong, J. Polym. Science, 54 (1961), pp. 385-410.

A particularly important commercial specie of polyester so produced is polyethylene terephthalate (PET).

[00026] In addition to catalyzing polycondensation reactions, the synergistic catalyst combinations of the present invention are effective for catalyzing esterification and transesterification reactions when used in catalytically effective amounts with reactants known to participate in esterification or transesterification reactions. A catalytically effective amount is suitable.

[00027] An improved three component enhanced catalyst composition can be obtained by the addition of second catalyst to enhanced catalyst composition defined above, the second catalyst being a compound containing antimony or germanium.

[00028] TITANIUM OXALATE CATALYSTS: Examples of titanium oxalate catalysts of the formula $X_m\text{TiO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_n$, where each X is independently selected from the group consisting of H, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and ammonium, $m=1$ or 2 are well known. Titanyl oxalates comprise compounds of the formula: $X_m\text{TiO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_n$, where X is selected from the group consisting of: H, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr and Ba, $m=1$ or 2 . Titanyl oxalates include metallic titanyl oxalates of the formula $M_2\text{TiO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_n$ wherein each M is independently selected from potassium, lithium, sodium and cesium such as lithium or potassium titanyl oxalate and nonmetallic titanyl oxalates such as ammonium titanyl oxalate. The titanyl oxalate may be anhydrous ($n=0$) or contain some water of hydration, i.e. n representing the amount of water of hydration. Preferred are H, Li, Na, K, Ca, Cs and ammonium.

[00029] CARBOXYLIC ACID OR SALT: Examples of a catalyst enhancer for the titanium oxalate catalysts are a carboxylic acid containing 1 to 26 carbon atoms or its corresponding carboxylic acid salt having an anion selected from the group consisting of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and ammonium. As used herein, "carboxylic acid" includes dicarboxylic acid. Examples of such carboxylic acids or salts are well known and include sodium acetate, sodium propionate, sodium citrate, sodium butyrate, sodium formate, sodium fumarate, malonic acid, potassium acetate, potassium benzoate, succinic acid, glutaric acid, adipic acid, maleic acid. Preferred are potassium acetate, potassium benzoate.

[00030] TITANIUM CONTAINING CATALYSTS: Examples of titanium containing compounds of the formula X_mTiY_o with X selected from the group consisting of: H, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and ammonium, $m=0, 1$, or 2 , Y is a ligand of the formula $C_aH_bO_c$, $a=0$ to 30 , $b=0$ to 60 , and $c=1$ to 10 ; $o=2, 3, 4$, include: acetylacetonate ($a=5$, $b=7$, and $c=2$); i-propoxide ($a=3$, $b=7$, and $c=1$); butoxide ($a=4$, $b=9$, and $c=1$); bis(2,2,6,6,-tetramethy-3,5-heptanedionato), i.e. $a=11$, $b=19$, and $c=2$. Preferred are acetylacetonate, i-propoxide, bis(2,2,6,6,-tetramethy-3,5-heptanedionato).

[00031] OXALIC ACID OR SALT: Examples of a catalyst enhancer for said titanium containing compounds are oxalic acids or its corresponding Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, or ammonium oxalic acid. Preferred are H, Li, Na, K, Ca, Cs, and ammonium.

[00032] ANTIMONY CONTAINING CATALYSTS: Examples of antimony containing catalysts that can be added to the synergistic combination of enhanced titanium oxalate or titanium containing catalysts defined above are Sb_2O_3 , $Sb(CH_3COO)_3$, and $Sb_2(OCH_2CH_2O)_3$.

[00033] GERMANIUM CONTAINING CATALYSTS: Examples of germanium containing catalysts that can be added to the synergistic combination of enhanced titanium oxalate or titanium containing catalysts defined above are GeO_2 , $Ge(OC_2H_5)_4$, $Ge[OCH(CH_3)_2]_4$, $Ge(OCH_3)_4$. Preferred is GeO_2 .

[00034] ENHANCEABLE ANTIMONY CONTAINING CATALYSTS: Examples of antimony containing catalysts that can be enhanced with a carboxylic acid or salt or an oxalic acid or salt are Sb_2O_3 , $Sb(CH_3COO)_3$, $Sb_2(OCH_2CH_2O)_3$.

[00035] Cocatalyst: Cocatalysts that function in combination with the titanium containing catalyst and the enhancer include antimony triacetate, $Sb(CH_3COO)_3$, antimony glycoxide, $Sb_2(OCH_2CH_2O)_3$, antimony oxide, (Sb_2O_3) .

[00036] An effective amount for enhancing the catalytic activity of titanyl oxalate catalysts or a titanium containing catalyst is at least about 0.1 part of enhancer per part of titanyl oxalate catalyst. Preferred is from about 0.1 part to about 100 parts enhancer per part of catalyst based upon the total weight of titanium in the catalyst.

[00037] When used in combination with an enhancer, a catalytically effective amount of titanium containing catalyst should be added to the polyester forming reactants, generally

at least 0.1 part based upon the weight of titanium. Preferred is from about 1 part to about 40 parts per million of catalyst based on the weight titanium in the catalyst and the weight of the of polyester forming reactants.

[00038] When used in combination with an enhancer, a catalytically effective amount of an antimony containing catalyst should be added to the polyester forming reactants. Preferred is from about 1 part to about 240 parts per million of catalyst based on the weight antimony in the catalyst and the weight of the of polyester forming reactants. For enhancing an antimony containing catalyst, an effective amount for of an enhancer for the catalytic activity of an antimony containing catalyst is at least about 0.1 part of enhancer per part of antimony containing catalyst based the weight of antimony in said antimony containing catalyst. Preferred is from about 0.1 part to about 80 parts enhancer per part of catalyst based upon the total weight of titanium in the catalyst.

[00039] The preferred amount of a antimony or germanium containing catalyst for use in combination with the enhanced titanium oxalate or titanium containing catalyst described above is from about 0.1 parts to about 80 parts based upon the weight of titanium. Preferred is from 1 to 40 parts of antimony or germanium containing catalyst.

[00040] The catalyst and enhancer mixtures of the present invention are used to make polyester typically by first dissolving them in a solvent that is compatible with polyester forming reactants, or preferable in one of the reactants itself, such as ethylene glycol.

[00041] The synergistic performance of the catalyst enhancer in combination with one or more catalysts for a polycondensation reaction for the production of PET resin is shown by the following examples.

Examples

[00042] In a polyester polycondensation reaction, acetaldehyde (AA) is an undesirable polymerization by-product. Polymerization rate is measured as rate at which intrinsic viscosity (IV) increases during reaction. Intrinsic viscosity change is an indication of the degree of polymerization that has occurred during the reaction.

Examples 1-20 and A-G

[00043] Catalyst evaluation was performed with a 3/16 stainless steel, 2 L reactor, fitted with a ball valve at the bottom of the reactor. The vessel was equipped with 3 inlet ports, one outlet port, one thermowell port and one pressure transducer port, and was vertically stirred by an electric motor with amperage monitoring. The laboratory experimental were all conducted on a 4.0 mole scale, using as polyester forming reactants, BHET and a normal bottle resin autoclave recipe. The experimental catalysts were added at the time of BHET charging.

[00044] Bis(2-hydroxyethyl)terephthalate (BHET) and catalyst were added to the reactor and the contents blanketed with nitrogen. The mixtures were heated under reduced pressure with constant stirring. The ethylene glycol (EG) produced during the polymerization was removed and trapped. The polymerization was at 280°C, under the vacuum of typically around 1 torr. The reaction was terminated when the stirrer torque reached a level, indicated by amperage to the stirrer motor, typical for a polymer of IV ~0.6. The molten state polymer under nitrogen (containing less than 2 ppm of oxygen) blanket was discharged from the bottom ball valve and quenched into a bucket filled with cold water. 1/4" diameter and 1/16" thick pellets (for color measurement) were made by filling the molten polymer in a press molder and chilled immediately in cold water.

[00045] The solution intrinsic viscosity (IV) was measured by following the ASTM D 4603 method. Acetaldehyde (AA) was measured at 150°C using gas chromatography (GC) equipped with a headspace analyzer. The brightness (L*) and yellowness (b*) were determined by the Hunter Lab's instrument and method.

[00046] Twenty-seven examples were performed using the above procedure and various catalysts and catalyst enhancer amounts.

[00047] Example A catalyst - 180 ppm potassium oxalate - reaction time = 124 mins.

[00048] Example B catalyst - 2 ppm titanium from potassium titanyl oxalate - reaction time = 118 mins.

[00049] Example C catalyst - 6 ppm titanium potassium titanyl oxalate - reaction time = 71 mins.

- [00050] Example D catalyst - 25 ppm antimony from antimony (III) oxide - reaction time = 122 mins.
- [00051] Example 1 catalyst - 2 ppm titanium from potassium titanyl oxalate + 90 ppm potassium oxalate - reaction time = 111 mins.
- [00052] Example 2 catalyst - 90 ppm potassium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 120 mins.
- [00053] Example 3 catalyst - 180 ppm potassium oxalate + 50 ppm antimony from antimony (III) oxide - reaction time = 130 mins.
- [00054] Example 4 catalyst - 90 ppm potassium oxalate + 100 ppm antimony from antimony (III) oxide - reaction time = 112 mins.
- [00055] Example 5 catalyst - 2 ppm titanium from potassium titanyl oxalate + 90 ppm potassium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 105 mins.
- [00056] Example E catalyst - 240 ppm antimony from antimony (III) oxide - reaction time = 90 mins.
- [00057] Example F catalyst - 240 ppm antimony from antimony (III) oxide - reaction time = 100 mins.
- [00058] Example 6 catalyst - 2 ppm titanium from potassium titanyl oxalate + 90 ppm potassium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 73 mins.
- [00059] Example 7 catalyst - 2 ppm titanium from potassium titanyl oxalate + 90 ppm ammonium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 78 mins.
- [00060] Example 8 catalyst - 2 ppm titanium from ammonium titanyl oxalate + 90 ppm potassium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 79 mins.
- [00061] Example 9 catalyst - 2 ppm titanium from ammonium titanyl oxalate + 90 ppm ammonium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 77 mins.

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- [00062] Example 10 catalyst - 2 ppm titanium from potassium titanyl oxalate + 90 ppm potassium acetate + 25 ppm antimony from antimony (III) oxide - reaction time = 81 mins.
- [00063] Example 11 catalyst - 2 ppm titanium from potassium titanyl oxalate + 90 ppm potassium benzoate + 25 ppm antimony from antimony (III) oxide - reaction time = 72 mins.
- [00064] Example 12 catalyst - 2 ppm titanium from bis(2,2,6,6-tetramethyl-3,5-heptanedionato) oxotitanium + 90 ppm potassium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 72 mins.
- [00065] Example 13 catalyst - 2 ppm titanium from di(i-propoxide)bis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium + 90 ppm potassium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 100 mins.
- [00066] Example 14 catalyst - 2 ppm titanium from titanium oxide acetylacetonate + 90 ppm potassium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 114 mins.
- [00067] Example 15 catalyst - 2 ppm titanium from potassium titanyl oxalate + 90 ppm calcium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 109 mins.
- [00068] Example 16 catalyst - 2 ppm titanium from potassium titanyl oxalate + 45 ppm oxalic acid + 25 ppm antimony from antimony (III) oxide - reaction time = 108 mins.
- [00069] Example 17 catalyst - 2 ppm titanium from potassium titanyl oxalate + 90 ppm sodium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 108 mins.
- [00070] Example 18 catalyst - 2 ppm titanium from lithium titanyl oxalate + 50 ppm lithium oxalate + 25 ppm antimony from antimony (III) oxide - reaction time = 102 mins.
- [00071] Example G catalyst - 60 ppm germanium from germanium oxide - reaction time = 149.
- [00072] Example 19 catalyst - 10 ppm germanium from germanium oxide + 90 ppm potassium oxalate - reaction time = 130 mins.

[00073] Example 20 catalyst - 2 ppm titanium from potassium titanyl oxalate + 90 ppm potassium oxalate + 7 ppm germanium from germanium oxide - reaction time = 123 minutes.

Example Results and Discussion

EXAMPLE	AMOUNT (mg)	POLY TIME (mins.)	IV	AA (ppm)	L*	b*
A	185.5	124	0.252	66.1	80.3	3.6
B	15.4	118	0.583	52.9	76.6	8.3
C	46.5	71	0.583	42.7	78.4	7.1
D	30.8	122	0.230	53.7	na	na
1	106.4	111	0.591	52.6	76.6	7.7
2	125.9	120	0.461	24.4	68.3	5.8
3	246.8	130	0.536	46.1	80.4	6.5
4	215.6	112	0.587	38.3	77.6	6.0
5	137.0	105	0.596	42.4	81.4	5.3
E	298.9	90	0.593	34.9	69.9	5.3
F	296.7	100	0.586	34.3	70.0	5.9
6	137.2	73	0.514	26.8	79.6	3.4
7	137.6	78	0.520	32.4	77.3	4.7
8	133.6	79	0.519	33.8	80.4	4.1
9	134.2	77	0.542	12.4	78.6	5.6
10	137.1	81	0.538	22.0	78.3	5.3
11	208.9	72	0.534	18.2	75.5	6.1
12	140.7	72	0.540	19.9	66.4	5.2
13	145.5	100	0.590	45.6	65.7	5.2
14	134.3	114	0.589	42.9	71.9	6.8
15	137.9	109	0.597	42.9	78.3	6.2
16	92.7	108	0.607	39.7	76.2	6.9
17	137.5	108	0.600	43.0	80.8	5.0
18	95.7	102	0.583	37.7	80.4	5.9
G	89.8	149	0.586	43.9	79.9	5.1
19	106.3	130	0.494	41.3	64.9	3.7
20	117.9	123	0.583	42.5	74.1	8.4

[00074] In comparing examples A, B, C and 1, 180 ppm potassium oxalate alone produced a polymer with a IV of 0.252 after 124 minutes. Using example B as a baseline, to a polymer with a similar IV, 118 minutes were needed for 2 ppm titanium in potassium titanyl oxalate while only 71 minutes were needed for 6 ppm titanium as shown in example

C. The addition of potassium oxalate to potassium titanyl oxalate enhanced the rate of polymerization as can be seen in example 1.

[00075] In comparing examples A, D, 2, 3, 4 E and F, 180 ppm potassium oxalate alone produced a polymer with an IV of 0.252 after 124 minutes, 25 ppm of antimony in antimony oxide produced a polymer with an IV of 0.230 after 122 minutes. It is shown in examples 2, 3, and 4 that the addition of potassium oxalate to antimony enhanced the polymerization rate, reduced the amount of acetaldehyde, and also increased the brightness as compared to examples E and F.

[00076] In comparing examples B and 5, using the combination of potassium titanyl oxalate, potassium oxalate, and antimony oxide, the polymerization rate was faster, the acetaldehyde concentration was lower, the resulting polymer was more brighter and less yellow.

[00077] In comparing examples 5, E and F, the three component catalyst produced more brighter and less yellow polymer than antimony oxide. It is conceivable that the rate for three components can be further enhanced and the amount of acetaldehyde in the resulting polymer can be further reduced by adjusting the composition of the three components.

[00078] In comparing examples 6 to 9, replacing potassium with ammonium in three components catalyst reduced the polymerization rate slightly. The resulting polymer by ammonium containing catalyst was slightly more yellow.

[00079] In comparing examples 5, 6, 10 to 14, different ligands such as oxalate, acetate, benzoate, bis 2,2,6,6-tetramethyl-3,5-heptanedionate, i-propoxide, acetylacetonate have been used. The catalysts containing these ligands polymerized BHET in a comparable rate with oxalate containing catalyst. However, the polymers using catalyst containing ligands rather than oxalate were less bright and more yellow. Therefore, the oxalate embodiment of the present invention is preferred over the ligand containing embodiment of the invention.

[00080] In comparing examples 5, 15 to 18, although catalysts containing H, Li, Na, K, and Ca can polymerize BHET in a similar rate, Li containing catalyst produced the least amount of acetaldehyde in the resulting polymer and are therefore preferred.

[00081] In comparing examples G, 19 and 20, the germanium catalyst can be enhanced by potassium oxalate.

We claim:

1. A catalyst combination comprising a titanyl oxalate of the formula $X_mTiO(C_2O_4)_2(H_2O)_n$, where each X is independently selected from the group consisting of : H, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, and ammonium $m=1$ or 2 and a catalyst enhancer comprising oxalic or carboxylic acid containing 1 to 26 carbon atoms or their corresponding Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba or ammonium salt.
2. An enhanced catalyst comprising a titanium compound of the formula X_mTiY_o , X is selected from the group consisting of: H, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and ammonium, $m=1$ or 2, Y is a ligand of the formula $C_aH_bO_c$, $a=0$ to 30, $b=0$ to 60, and $c=1$ to 10; $o=2, 3, 4$, and a catalyst enhancer of an oxalic acid or its corresponding Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba or ammonium salt.
3. The catalyst of claim 1 further comprising an additional catalyst enhancer of a compound containing antimony or germanium.
4. The catalyst of claim 2 further comprising an additional catalyst enhancer of a compound containing antimony or germanium.
5. An enhanced catalyst combination comprising an antimony containing catalyst and a catalyst enhancer of oxalic acid or its corresponding Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba or ammonium salt.
6. An enhanced catalyst combination comprising a germanium containing catalyst and a catalyst enhancer of oxalic acid or its corresponding Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba or ammonium salt.
7. The catalyst combination of any of claims 1 through 4 wherein the concentration of titanium is from 0.1 to 100 ppm.
8. The combination of claim 1 wherein the catalyst enhancer is selected from the

group consisting of lithium titanyl oxalate, potassium titanyl oxalate and ammonium titanyl oxalate.

9. The combination of claim 2 wherein the catalyst enhancer is selected from the group consisting of lithium oxalate, $\text{Li}_2\text{C}_2\text{O}_4$, sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, potassium oxalate, $\text{K}_2\text{C}_2\text{O}_4$, rubidium oxalate, $\text{Rb}_2\text{C}_2\text{O}_4$, and cesium oxalate, $\text{Cs}_2\text{C}_2\text{O}_4$.
10. The combination of claim 1 wherein the titanyl oxalate is selected from the group consisting of metallic titanyl oxalates of the formula $\text{M}_2\text{TiO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_n$ wherein each M is independently selected from potassium, lithium, sodium, cesium and a nonmetallic cation such as ammonium.
11. The combination of claim 1 wherein the catalyst enhancer is lithium oxalate and the titanyl oxalate is lithium titanyl oxalate.
12. The combination of claim 5 wherein the antimony containing catalyst is selected from the group consisting of antimony triacetate, $\text{Sb}(\text{CH}_3\text{COO})_3$, antimony trisglycoxide; $\text{Sb}_2(\text{OCH}_2\text{CH}_2\text{O})_3$, antimony oxide (Sb_2O_3).
13. The combination of claim 1, wherein the catalyst enhancer oxalate comprises from 0.1 part to 80 parts by weight of the combination based upon the weight of titanium.
14. The combination of claim 2, wherein the catalyst enhancer comprises from 0.1 part to 80 parts by weight of the combination based upon the weight of titanium.
15. The combination of claim 5, wherein the catalyst enhancer comprises from 0.1 part to 80 parts by weight of the combination based upon the weight of antimony.
16. The combination of claim 6, wherein the catalyst enhancer comprises from 0.1 part to 80 parts by weight of the combination based upon the weight of germanium.

17. The combination of claim 3, wherein the enhancer comprises from 0.1 part to 80 parts by weight of the composition.
18. The combination of claim 4, wherein the enhancer comprises from 0.1 part to 80 parts by weight of the composition.
19. An improved process of producing a polyester by the catalyzed polycondensation of polyester forming reactants in the presence of a polycondensation catalyst, wherein the improvement comprises utilizing as the catalyst the combination of claim 1.
20. An improved process of producing a polyester by the catalyzed polycondensation of polyester forming reactants in the presence of a polycondensation catalyst, wherein the improvement comprises utilizing as the catalyst the combination of claim 2.
21. An improved process of producing a polyester by the catalyzed polycondensation of polyester forming reactants in the presence of a polycondensation catalyst, wherein the improvement comprises utilizing as the catalyst the combination of claim 5.
22. An improved process of producing a polyester by the catalyzed polycondensation of polyester forming reactants in the presence of a polycondensation catalyst, wherein the improvement comprises utilizing as the catalyst the combination of claim 6.
23. An improved process of producing a polyester by the catalyzed polycondensation of polyester forming reactants in the presence of a polycondensation catalyst, wherein the improvement comprises utilizing as the catalyst the combination of claim 7.
24. An improved process of producing a polyester by the catalyzed polycondensation of polyester forming reactants in the presence of a polycondensation catalyst, wherein the improvement comprises utilizing as the catalyst the combination of claim 9.
25. An improved polyester containing the combination of claim 1.

26. The improved polyester of claim 24 wherein the catalyst combination comprises from 0.1 part to 80 parts per million of the polyester.
27. The improved polyester produced by the process of claim 19.
28. An improved polyester containing the composition of claim 2.
29. The improved polyester of claim 24 wherein the polyester is polyethylene terephthalate.
30. The combination of claim 1 dissolved in a solvent
31. The combination of claim 30 wherein the solvent is ethylene glycol.

Abstract of the Invention

The present invention is based upon the discovery that nontitanyl oxalates can enhance the catalytic functionality of titanyl oxalate catalysts. This invention provides a novel catalytic composition containing a titanyl oxalate catalyst and a metallic oxalate catalyst enhancer and optionally containing a metallic cocatalyst such as an antimony based catalyst. A synergistic relationship has been discovered between titanyl oxalate catalyst and the catalyst enhancer. A synergistic relationship has also been discovered between the titanyl oxalate catalyst, catalyst enhancer and a metallic cocatalyst such as antimony oxide or antimony triacetate. Also provided is an improved process of producing polyester by the polycondensation of polyester forming reactants in the presence of a catalytically effective amount of a polycondensation catalyst, wherein the improvement comprises utilizing, as the polycondensation catalyst, the novel catalyst composition containing a titanyl oxalate such as lithium titanyl oxalate and a catalyst enhancer such as a nontitanyl metallic oxalate like lithium oxalate and optionally containing a metallic catalyst such as antimony oxide or antimony triacetate. The improved process produces an improved polyester having lower acetaldehyde numbers and good color. The titanyl oxalate/catalyst enhancer composition can be used as a polycondensation catalyst in combination with other catalysts to achieve synergistic catalytic activity. Preferred is a combination of lithium or potassium titanyl oxalate, Li_2 or $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$, lithium or potassium oxalate, Li_2 or $\text{K}_2(\text{C}_2\text{O}_4)_2$ with antimony oxide or antimony triacetate or antimony trisglycoxide.

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CONSULADO GENERAL DE COLOMBIA

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EL SUSCRITO CONSUL DE COLOMBIA

VISTOS LOS DOCUMENTOS PRESENTADOS POR LOS INTERESADOS

CERTIFICA

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AUG 25 2000

Que el (la) Sr. **KIM PIZZINGRILLI**, Secretaria de la Commonwealth de Pennsylvania, verificó la firma de el (la) señor(a) **GERALDINE M. MCMENAMIN**, como notario (a) Público (a) del mismo condado, quien ejerce las funciones allí expresadas y que la firma y sello que aparecen en el documento anexo, son los que usa y acostumbra en sus actos oficiales.

Que el Notario arriba mencionada verificó la firma del señor(a) **MARY G. FAY**, Quien firma el precedente documento debidamente autorizado en calidad de Secretaria Asistente de la sociedad **ATOFINA CHEMICALS, INC.** Sociedad legalmente organizada y existente bajo las leyes del Estado de Pennsylvania, U.S.A.

Que ha tenido a la vista los documentos probatorios de los hechos citados anteriormente, los cuales forman parte integral del precedente documento.

Se expide la anterior certificación de conformidad con el artículo 259 del Código de Procedimiento Civil y 480 del Código de Comercio a solicitud del interesado a los 25 días del mes de Agosto del 2000.

NO SE ASUME RESPONSABILIDAD POR EL CONTENIDO DEL DOCUMENTO ADJUNTO.

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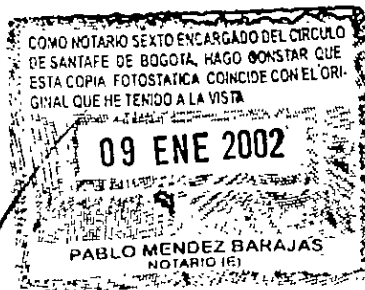
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COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF STATE

Cert. No. 0018920

OFFICE OF THE SECRETARY OF THE COMMONWEALTH

Harrisburg, August 10, 2000

PENNSYLVANIA, SS:

I, Kim Pizzingrilli, Secretary of the Commonwealth of Pennsylvania, DO HEREBY CERTIFY, That it appears by the records of this office that

Geraldine M. McMenamain

whose official attestation appears upon the attached instrument, was at the time of signing the same, an acting **Notary Public** in and for the Commonwealth of Pennsylvania, U.S.A., with registered office in the

City of Philadelphia, Philadelphia County

duly appointed, commissioned and qualified, and as such officer had power within said Commonwealth, to administer oaths and affirmations, to make declarations and protests, take depositions and affidavits, take and receive the acknowledgement of proof of all deeds, conveyances, mortgages and other instruments of writing, touching or concerning any lands, tenements or hereditament situate, lying or being in any part of said State, receive the proof or acknowledgement of all instruments of writing relating to commerce or navigation, letters of attorney, and such other writings as have been usually proved or acknowledged before notaries within said Commonwealth, etc., according to law, in all matters belonging or incident to the exercise of notarial office, and accordingly full faith and credit are due and ought to be given to the official acts of said notary; That I verily believe the seal and signature attesting the same are genuine.

IN TESTIMONY WHEREOF, I have hereunto set my hand and caused the seal of my Office to be affixed, the day and year above written.



Kim Pizzingrilli
Secretary of the Commonwealth
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Traductora e Intérprete Oficial
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Representation and Poder- of- Attorney with con certificado notarial for patents, utility models, industrial designs, trademarks, commercial names, trade emblems, slogans, licenses.



REPRESENTATION AND POWER- OF- ATTORNEY

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I (we), the undersigned ATOFINA CHEMICALS, INC.

of 2000 Market Street
Philadelphia, PA 19103-3222, U.S.A.

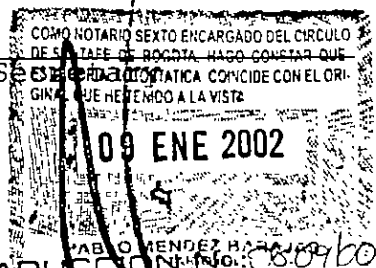
do hereby appoint EMILIO FERRERO, T.P.A. N° 31.929; GONZALO PERDOMO, T.P.A. N° 831; LUZ CLEMENCIA DE PAEZ, T.P.A. N° 23.555 and GERMAN CAVELIER, T.P.A. N° 832, domiciled at Carrera 4a. No. 72-35, Bogotá, Colombia, in due compliance with the terms of Paragraph 1st. of Article 543 of the Commercial Code, the first as principal and the others as alternates, in the order of their appointment, as our representatives for all industrial property matters, with faculty to accept notifications and to appoint attorneys in and out of Court. The first alternate shall replace the principal in case of his absence or of temporal or definitive impediment. The same rule shall apply when the second alternate representative is to replace the first one, or when the third is to replace the second. In such cases, the principal representative, or the first or second alternates in their turn, or both of them, shall state their intention not to act as representatives through a declaration given before a Notary Public, or another Public Official, or a Colombian Consul abroad; and in case of impediment, the appropriate certificate shall suffice. If any of the appointees were to be definitely absent, the following alternate shall take his place. When the absence or impediment of the principal, or of the first, or second alternates in their turn ceases, the representation can be taken again by the principal, the first or second alternates depending on case, and the mere fact of its exercise shall suffice for the representation to be fully valid. The exercise of the representation by the first, second or third alternates in their turn shall end at such time.

In addition we grant a Power of Attorney in favor of the above-named attorneys-at-law so that they may obtain the protection of my (our) industrial property and against unfair competition, for which purpose I (we) authorize the said attorneys to represent me (us) before any authorities or persons, with or without jurisdiction, especially those administrative, administrative contentious and judicial, as well as before Arbitration Court, in all matters concerning the following: a) Obtainment of patents, utility models and industrial designs; the registration of trademarks, collective, defensive and service marks, slogans, commercial names, trade emblems, vegetal varieties and denominations of origin; its renewal, assignment, change of name or domicile, voluntary cancellation, and the registration of licenses of use of the above rights; b) Actions of unfair competition, protection to the consumer, oppositions or observations, administrative or Court cancellation, nullity, infringement, granting of licenses, the action for writ mandamus, the protection of trade secrets, and in general the civil, penal and administrative suits relating to those rights; actions and suits instituted by me (us) or against me (us). And that in all the above matters they may substitute this Power of Attorney, compromise, conciliate, admit the facts of the case, desist, cancel, receive, resign and ratify acts done by representatives without a power of attorney.

Given and signed this July 26, 2000

in Philadelphia, Pennsylvania, U.S.A.

By *Mary G. Fay*
Mary G. Fay, Assistant Secretary



ABO RENEZ BARRAJON
TRADUCCION No. 680760
MARIA ELVIRA MARTÍNEZ
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2879 Min. Justicia

CERTIFICADO NOTARIAL (INDIVIDUO)

A los ____ días del mes de _____ de 200__

ante mí, Notario Público o Funcionario Autorizado de _____

_____ compareció(eron) personalmente

a quien(es) doy fe de conocer y me consta que es(son) la(s) persona(s) firmante(s) del documento que precede, y quien(es) tiene(n) capacidad legal para otorgarlo.

Notario Público o Funcionario Autorizado — Notary Public or Attesting Official

CERTIFICADO NOTARIAL (SOCIEDAD)

Hoy, 26 de Julio de 2000

compareció(eron) ante mí

MARY G. FAY

a quien(es) conozco personalmente y que firma(n) este documento en representación de la Sociedad/compañía

denominada ATOFINA CHEMICALS, INC.

Certifico:

1. Que he visto los siguientes documentos:*

RESOLUCION DE LA JUNTA DIRECTIVE FECHADO
15 DICIEMBRE, 1999.

2. Que dichos documentos prueban lo siguiente:

2.1. Que ATOFINA CHEMICALS, INC.

es una Sociedad/Compañía legalmente constituida y existente

de acuerdo con las leyes de Estado de Pennsylvania,
Estados Unidos de América

2.2. Que el domicilio de dicha Sociedad/Compañía es

Philadelphia, PA 19103-3222, E.U.A.

2.3. Que el objeto u objeto para los cuales se otorga el presente poder están comprendidos dentro del objeto social de la mencionada Sociedad/Compañía.

2.4. Que el(los) Sr.(Sres.) MARY G. FAY

está(n) autorizado(s) para otorgar el presente Poder.

Ciudad PHILADELPHIA

Estado PENNSYLVANIA

Hoy 26 JULIO de 2000

Geraldine M. McMenamin

Notario Público o Funcionario Autorizado — Notary Public or Attesting Official

* Los documentos deben identificarse con fecha y origen.

Notarial Seal
Geraldine M. McMenamin, Notary Public
Philadelphia, Philadelphia County
My Commission Expires Aug. 24, 2002

Member, Pennsylvania Association of Notaries

NOTARIAL CERTIFICATE (INDIVIDUAL)

On this ____ day of _____ 200__

before me, a Notary Public or Attesting Official of _____

_____ personally appeared

to me known, and known to me to be the person(s) who executed that foregoing document, and who has(have) legal capacity to execute it.

Notary Public or Attesting Official

NOTARIAL CERTIFICATE (CORPORATION)

On this 26 day of July 2000

appeared before me

Mary G. Fay

who(m) I know personally and who(m) signed this document as representative(s) of the Corporation/Company

named ATOFINA CHEMICALS, INC.

I Certify:

1. That I have seen the following documents:*

Board of Directors Resolution
dated December 15, 1999

2. That the above documents duly prove the following:

2.1. That ATOFINA CHEMICALS, INC.

is a Corporation/Company legally constituted and in existence

in accordance with the laws of State of Pennsylvania,
United States of America

2.2. That the domicile of said Corporation/Company is

Philadelphia, PA 19103-3222, U.S.A.

2.3. That the purpose of purposes for which the present Power of Attorney is granted are comprised within the corporation purposes set forth in the charter of the mentioned Corporation/Company.

2.4. That Mary G. Fay

is(are) authorized to grant the present Power of Attorney.

City Philadelphia

State Pennsylvania

This 26 day of July 2000

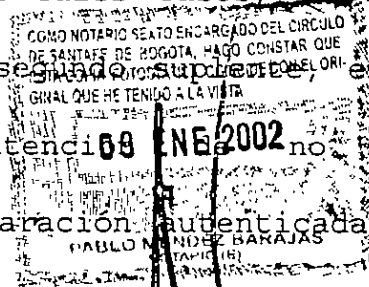
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PABLO MENDEZ BARAJAS
NOTARIO (E)

* Documents must be identified with date and origin.

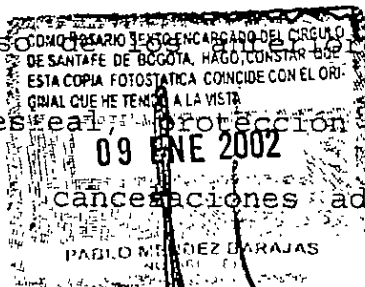
TRADUCCIÓN OFICIAL No. 08.09/00 preparada por María Elvira Martelo, Traductora Oficial debidamente aprobada por el Ministerio de Justicia de Colombia por Resolución 2879 de 1995 y reconocida por el Ministerio de Relaciones Exteriores.

Yo (nosotros) el/los abajo firmante(s) **ATOFINA CHEMICALS, INC.** ubicada en 2000 Market Street, Philadelphia, PA 19103-3222, Estados Unidos de América, por el presente nombramos a **EMILIO FERRERO**, tpa. No. 31929; **GONZALO PERDOMO**, tpa. No. 831; **LUZ CLEMENCIA DE PAEZ**, tpa. No. 23.555, Y **GERMAN CAVELIER**, tpa. No. 832, domiciliados en la Carrera 4ª N° 72-35, Bogotá, Colombia, en obediencia a lo dispuesto en el parágrafo 1º del Artículo 543 del Código de Comercio, el primero como principal y los demás como suplentes, en el orden de nombramiento, como nuestros representantes en todos los asuntos de propiedad industrial con facultad para recibir notificaciones y nombrar apoderados judiciales y extrajudiciales. El primer representante suplente reemplazará al principal en caso de ausencia o impedimento temporal o definitivo de aquel. La misma regla se aplicará cuando el segundo representante suplente haya de reemplazar al primero, o el tercero al segundo. En tales casos, el representante principal, o el primero, o segundo suplente, en su caso, o ambos, declararán su intención de ejercer la representación mediante declaración autenticada por Notario Público en Colombia, o por Notario y otro Funcionario Público o Cónsul de Colombia, en el extranjero, y si se tratare de



impedimento, con el certificado respectivo. Si alguno de los nombrados faltare definitivamente, el siguiente tomará su lugar. Cuando cesare la ausencia o impedimento del representante principal, o de su primer o segundo suplente, en su caso, la representación la podrá tomar de nuevo el principal, el primero o el segundo suplente según el caso, y el mero hecho de su ejercicio será suficiente para que la representación sea totalmente válida. El ejercicio de la representación por el primero, segundo o tercer suplente, a su vez, terminará en ese momento.

Además, conferimos poder a los abogados arriba nombrados para obtener la protección de nuestra propiedad industrial y contra la competencia desleal, a cuyo efecto autorizamos a dichos apoderados para que nos representen ante cualquier entidad o persona, ejerzan o no jurisdicción, especialmente ante las de orden administrativo,, contenciosos-administrativo y judicial, así como ante Tribunal de Arbitramento, en todo lo concerniente a los siguientes asuntos: a) Obtención de patentes, modelos de utilidad y diseños industriales; el registro de marcas comerciales, de marcas colectivas, defensivas y de servicio, lemas, nombres comerciales, emblemas comerciales, variedades vegetales y denominaciones de origen; su renovación, cesión, cambio de nombre o domicilio, cancelación voluntaria y el registro de licencias de uso de los derechos; b) Acciones de competencia desleal, protección al consumidor, oposiciones y observaciones, cancelaciones administrativas o



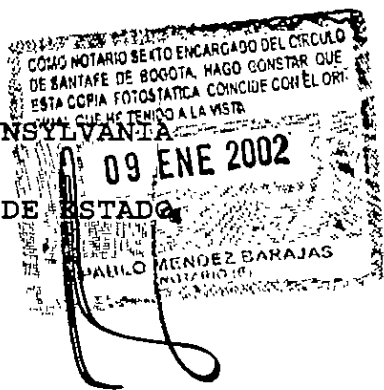
judiciales, nulidad, medidas cautelares, otorgamiento de licencias, acción de tutela, protección de secretos comerciales y en general los juicios civiles, penales y administrativos relacionados con esos derechos; acciones y juicios que promovamos o nos promuevan. Y en todos los asuntos arriba especificados, ellos pueden sustituir este mandato, transigir, desistir, cancelar, recibir, renunciar y ratificar los actos realizados por agentes oficiosos.

Dado y firmado hoy 26 de julio de 2000 en Filadelfia, Pennsylvania, EUA. Por: (Firma ilegible), Mary G. Fay, Secretario Asistente. (Sello seco) ATOFINA CHEMICALS, INC., Sello (ilegible).

(CERTIFICADO NOTARIAL - SOCIEDAD - otorgado en inglés y español en relación con la existencia legal de ATOFINA CHEMICALS, INC.) Expedido en la ciudad de Filadelfia, Estado de Pennsylvania, EUA, el 26 de julio de 2000. (Firma ilegible), Notario Público. (Sello notarial en tinta) SELLO NOTARIAL, Geraldine M. McMenamin, NOTARIO PÚBLICO, Filadelfia, Condado de Filadelfia. Mi comisión expira el 24 de agosto de 2002. (Sello seco) Geraldine M. McMenamin, Estado de Pennsylvania, Notario Público.

ESTADO DE PENNSYLVANIA
DEPARTAMENTO DE ESTADO

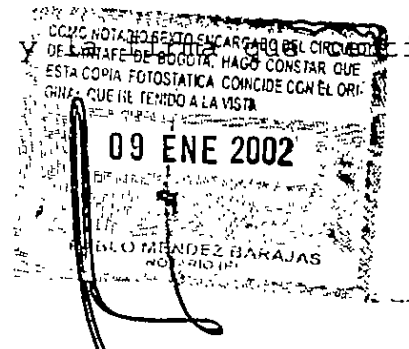
Cert. No. 0018920



SECRETARÍA DE ESTADO

Harrisburg, 10 de agosto de 2000

PENNSYLVANIA, SS:

Yo, Kim Pizzingrilli, Secretario del Estado de Pennsylvania, POR EL PRESENTE CERTIFICO que, de acuerdo con los registros de esta oficina, **Geraldine M. McMenamin**, cuya declaración oficial aparece en el instrumento adjunto, era en el momento de firmarla un **Notario Público** en y para el Estado de Pennsylvania, EUA, con oficina registrada en la **Ciudad de Filadelfia, Condado de Filadelfia**, debidamente nombrado, comisionado y calificado y como tal, tenía facultad dentro de dicho Estado, para tomar juramentos y afirmaciones, dar declaraciones y protestos, tomar declaraciones y declaraciones juramentadas, tomar y recibir reconocimientos de pruebas de todas las escrituras, traspasos, hipotecas y otros instrumentos escritos relacionados o tocantes a tierras, tenencias y heredades situadas en, o que forman parte de, dicho Estado, recibir la prueba o reconocimiento de todos los instrumentos escritos relacionados con el comercio o la navegación, poderes y otros escritos que normalmente se prueban ante notario dentro de dicho Estado, etc. de acuerdo con la ley, en todos los asuntos relacionados con, o incidentes al ejercicio del cargo notarial, y en consecuencia, a los actos oficiales de dicho Notario se les da y se les debe dar plena fe y crédito; que creo firmemente que el sello y  ifican el mismo son genuinos.

20

EN FE DE LO CUAL, he firmado y hecho imponer el sello de mi cargo en el día y año arriba indicados. (Firma facsimilar) Kim Pizzingrilli, Secretario de Estado. (Sello de oblea dorado) Secretario de Estado, Pennsylvania...

(En español) Certificación de la firma que antecede, de la existencia legal de ATOFINA CHEMICALS, INC., y de la capacidad legal de MARY G. FAY para otorgar el poder, expedida por el Consulado General de Colombia en Nueva York, el 25 de agosto de 2000, bajo el No. 255195/1. Firmado por JOSE DAVID NAME C., Cónsul de Colombia. Pagados impuestos de timbre y derechos consulares. (Sello consular en tinta).

(Al dorso) Legalización de la firma que antecede expedida por el MINISTERIO DE RELACIONES EXTERIORES bajo el No. 433386 del 12 de septiembre de 2000, firmado por el Jefe de Legalizaciones.

Es traducción fiel y completa de la cual se deja copia en esta oficina para su confrontación.

JOSE DAVID NAME C.
RESPONSABILIDAD DEL TEXTO
SEP 19 12:12:20
JEF. DE LEGALIZACIONES
SANTAFE DE BOGOTA D.C.

Maria E. Martelo
TRADUCCION No.: 0809100
MARIA ELVIRA MARTELO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2879 Min. Justicia

MINISTERIO DE RELACIONES EXTERIORES
534858
GUAYAMA MARTELO
RECONOCIMIENTO DE SEMPRE
LAS FIRMAS INDICADAS

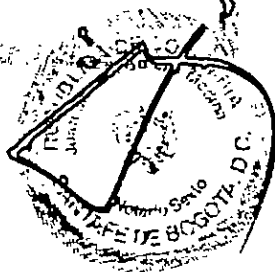
COMO NOTARIO SEXTO ENCARGADO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA
09 ENE 2002
PARLO MENDEZ BARAJAS
NOTARIO (E)

COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE LA(S) FIRMA(S) DE

[Handwritten signature]

COINCIDE(N) CON LA FIRMA REGISTRADA POR EL (ELLOS) EN ESTA NOTARIA

SANTAFE DE BOGOTA, 18 SET. 2000



COMO NOTARIO SEXTO ENCARGADO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE ESTA COPIA FOTOSTATICA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA

09 ENE 2002

PARLO MENDEZ BARAJAS
NOTARIO (S)

05-01-01-01-01-01

11-01-01-01-01-01

11-01-01-01-01-01

11-01-01-01-01-01



Industria y Comercio
SUPERINTENDENCIA

Radicacion : 02001352 0000/00 Folios: 34
Fecha (AMD): 2002-01-09 17:36:55
Tramite : 002 PATENTES D 1 REGISTRO/ 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

NIT : 900176089-2

RECIBO OFICIAL DE CAJA : 01 - 77,143
FECHA : DICIEMBRE 10 DE 2001

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	6482939	10/12/2001	8.429,480.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		1 TRAMITES DE SOL. DE PATENTE DE IN	356,640.00
		TOTAL :	356,640.00

SON: TRESCIENTOS CINCUENTA Y SEIS MIL SEISCIENTOS CUARENTA PESOS

21360
378000

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

Boleto 12362-801-003-5

Carrera 13 No. 27-00 Pisos 5, 7 y 10
Conmutador 382 0840
Fax 350 5220
E-mail: info@sic.gov.co
www.sic.gov.co
Bogotá, D.C., Colombia



Industria y Comercio

SUPERINTENDENCIA

NIT : 800176089-2

Radicacion : 00001352 00000000
 Fecha (AMD): 2002-01-09 16:36:55
 Trámite : 002 PATENTES D 1 REGISTRO/ 411 PRESENTAC
 Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Folios: 34

CERTIFICACION DE EXCEDENTE : 02 - 405
 FECHA : ENERO 8 DE 2002

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
PAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	4482963	08/01/2002	1,219,502.00

***** CONCEPTO *****

CANT.	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09 OTROS SERVICIOS DE PROPIEDAD I	
	99 OTROS SERVICIOS ADMINISTRATIVOS	21,360.00
	TOTAL :	\$ 21,360.00

CON: VEINTIUNO MIL TRESCIENTOS SESENTA PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

ESTA CERTIFICACION DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA
 COMO PARTE DE LA CANCELACION DE UNA TARIFA VIGENTE Y NO PODRA SER
 SUSTITUIDA POR NINGUN RECIBO.

Bo 17367-801-003-5

Carrera 13 No. 27-00 Pisos 5, 7 y 10
 Conmutador 382 0840
 Fax 350 5220
 E-mail: info@sic.gov.co
 www.sic.gov.co
 Bogotá, D.C., Colombia



Industria y Comercio

SUPERINTENDENCIA

Radicacion : 02001352 00000000
 Fecha (AMD): 2002-01-09 16:36:55
 Trámite : 002 PATENTES D 1 REGISTRO/ 411 PRESENTAR
 Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Folios: 34

NIT : 800174089-2

RECIBO OFICIAL DE CAJA : 01 - 77,111
 FECHA : DICIEMBRE 10 DE 2001

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	Nº. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	6482939	10/12/2001	8.429.480.00

***** CONCEPTO *****

CANT. REMTISTICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-01 SOLICITUDES	82 INVOCACION DE PRA PRIORITY EN NU	100.000.00
	TOTAL :	\$ 100.000.00

SON: CIENTO MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

010 12362-801-003-5

Carrera 13 No. 27-00 Pisos 5, 7 y 10
 Conmutador 382 0840
 Fax 350 5220
 E-mail: info@sic.gov.co
 www.sic.gov.co
 Bogotá, D.C., Colombia



Industria y Comercio
SUPERINTENDENCIA

NIT : 800176089-2

CERTIFICACION DE EXCEDENTE : 02 - 350
FECHA : ENERO 8 DE 2002

Radicacion : 02001352 00000000 Folios: 34
Fecha (AND): 2002-01-09 16:36:55
Tramite : 002 PATENTES D 1 REGISTRAD/ 411 REPRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	6482963	08/01/2002	1.219.502.00

***** CONCEPTO *****

CANT. CONTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09 OTROS SERVICIOS DE PROPIEDAD I 99 OTROS SERVICIOS ADMINISTRATIVOS	4.000.00
	TOTAL :	\$ 6.000.00

MON: SEIS MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

ESTA CERTIFICACION DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA
COMO PARTE DE LA CANCELACION DE UNA TARIFA VIGENTE Y NO PODRA SER
SUSTITUIDA POR NINGUN RECIBO.

Carrera 13 No. 27-00 Pisos 5, 7 y 10
Conmutador 382 0840
Fax 350 5220
E-mail: info@sic.gov.co
www.sic.gov.co
Bogotá, D.C., Colombia

Sl 12362-801-003-5

Radicacion : 02001352 00000000 Folios: 34
Fecha (AMD): 2002-01-09 16:36:55
Tramite : 002 PATENTES D 1 REGISTRO/ 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

REQUISITOS NECESARIOS PARA PRESENTAR

USUARIO RADICADOR

PATENTE DE INVENCION [X]

MODELO DE UTILIDAD

[] []

- Indicación de que se solicita la concesión de una patente [] [X]
- Datos de identificación del solicitante o de la persona que presenta la solicitud [] [X]
- Descripción de la invención [] [X]
- Dibujos de ser estos pertinentes [] []
- Comprobante de Pago de las tasas establecidas [] [X]

COMPLETA [X]

INCOMPLETA

[] []

DISEÑO INDUSTRIAL []

- Indicación de que se solicita el registro de Diseño Industrial. [] []
- Datos de identificación del solicitante o de la persona que presenta la solicitud. [] []
- Representación gráfica y fotográfica del Diseño Industrial o muestra del material que incorpora el diseño. [] []
- Comprobante de pago de las tasas establecidas. [] []

COMPLETA []

INCOMPLETA

[] []

ESQUEMA DE TRAZADO []

- Indicación de que se solicita el registro de un Esquema de trazado. [] []
- Datos de identificación del solicitante o de la persona que presenta la solicitud. [] []
- Representación gráfica del esquema de trazado [] []
- Comprobante de pago de las tasas establecidas. [] []

COMPLETA []

INCOMPLETA

[] []

Firma Responsable

Fecha:

Cartera No. 27-00 Piso 2 apartamento
Commutador 382 03 04
Tel. 01 52 20 ext. 1000000000
Bogotá D.C. Colombia

Folio 36

2020
Bogotá, D. C.

Doctor(a)
EMILIO FERRERO
Apoderado(a)

Oficio No. 09416

REFERENCIA: Radicación 02-1352
Trámite 002
Evento 001
Actuación 430
Folios 001

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica que:

- Debe allegar el documento en que consta la cesión del derecho a la patente otorgado por el inventor al solicitante o a su causante (art. 26-k, Dec 486/2000).
- Aportar la traducción de la solicitud presentada como solicitud colombiana

En cumplimiento del artículo 39 de la Decisión 486, en concordancia con el artículo 85 de la misma decisión, se le requiere para que dentro del término de dos (2) meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

Notifíquese el presente oficio conforme a lo dispuesto en el artículo 8 de la Resolución 210 del 15 de enero del 2001.

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista de fecha 14 MAR. 2002

Se recuerda al interesado que debe presentar, dentro de los dieciséis meses siguientes contados a partir de la fecha de presentación de la solicitud cuya prioridad se invoca, copia de la misma certificada por la autoridad que la expidió y, en los casos en que haya lugar, la traducción simple del capítulo reivindicatorio. El incumplimiento de éste plazo, acarreará la pérdida de la prioridad invocada.

202027