⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 397 454 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **90304952.6**

㉒ Date of filing: **08.05.90**

㉚ Priority: **08.05.89 US 348521**

㊸ Date of publication of application:
14.11.90 Bulletin 90/46

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(51) Int. Cl.⁵: **C23F 11/14**

(71) Applicant: **CALGON CORPORATION**
Route 60-Campbell's Run Road
Robinson Township Pennsylvania 15205(US)

(72) Inventor: **Vanderpool, Daniel P.**
109 Shippen Drive
Coraopolis, PA 15108(US)
Inventor: **Cha, Charles Y.**
123 Druid Drive
McMurray, PA 15317(US)

(74) Representative: **Hesketh, Alan, Dr. et al**
European Patent Department Merck & Co.,
Inc. Terlings Park Eastwick Road
Harlow Essex, CM20 2QR(GB)

(54) Higher alkylbenzotriazoles as copper and copper alloy corrosion inhibitors.

(57) Higher alkylbenzotriazoles are used to inhibit the corrosion of metallic surfaces in contact with an aqueous system. Systems and compositions containing higher alkylbenzotriazoles are also claimed.

HIGHER ALKYLBENZOTRIAZOLES AS NOVEL COPPER AND COPPER ALLOY CORROSION INHIBITORS

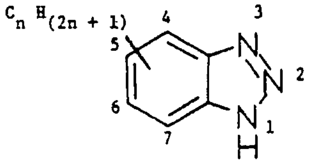
BACKGROUND OF THE INVENTION

Benzotriazole, mercaptobenzothiazole and tolyltriazole are well known copper corrosion inhibitors. For example, see U.S. patent 4,675,158 and the references cited therein. Also, see U.S. patent 4,744,950, which discloses the use of lower alkylbenzotriazoles as corrosion inhibitors and U.S. patent 4,406,811, which discloses the use of benzotriazole/tolyltriazole blends in water treatment compositions for multimetal corrosion inhibition.

The instant invention relates to the use of higher alkylbenzotriazoles as corrosion inhibitors, particularly copper and copper alloy corrosion inhibitors. These compounds from long-lasting protective films on metallic surfaces, particularly copper and copper alloy surfaces, in contact with aqueous systems.

DESCRIPTION OF THE INVENTION

The instant invention is directed to a method of inhibiting the corrosion of metallic surfaces, particularly copper and copper alloy surfaces, in contact with an aqueous system, comprising adding to the aqueous system being treated an effective amount of a higher alkylbenzotriazole compound having the following structure:



wherein n is greater than 6 and less than or equal to 12; and isomers of such compounds. Branched-chain C_6-C_{12} alkyls can also be used, though straight chain compounds are preferred as they are believed to provide more persistent films in the presence of chlorine.

The instant invention is also directed to an aqueous system which is in contact with a metallic surface, particularly a copper or copper alloy surface, and which contains a higher alkylbenzotriazole.

Compositions comprising water, particularly cooling water, and a higher alkylbenzotriazole are also claimed.

The inventors have discovered that higher alkylbenzotriazoles are effective corrosion inhibitors. These compounds form durable, long-lasting films on metallic surfaces, including but not limited to copper and copper alloy surfaces. Higher alkylbenzotriazoles are especially effective inhibitors of copper and copper alloy corrosion, and can be used to protect multimetal systems, especially those containing copper or a copper alloy and one or more other metals.

The instant inventors have also found that the instant alkylbenzotriazoles de-activate soluble copper ions, which prevent the galvanic deposition of copper which concomminantly occurs with the galvanic dissolution of iron or aluminum in the presence of copper ions. This minimizes aluminum and iron corrosion. These compounds also indirectly limit the above galvanic reaction by preventing the formation of soluble copper ions due to the corrosion of copper and copper alloys.

Isomers of the above described higher alkylbenzotriazoles can also be used. The 5 and 6 isomers are interchangeable by a simple prototropic shift of the 1 position hydrogen to the 3 position and are believed to be functionally equivalent. The 4 and 7 isomers are believed to function as well as or better than the 5 or 6 isomers, though they are more difficult and expensive to manufacture. As used herein, the term "higher alkylbenzotriazoles" is intended to mean 5-alkyl benzotriazoles and 4, 6 and 7 position isomers thereof, wherein the alkyl chain length is greater than 6 but less than or equal to 12 carbons, branched or straight, preferably straight.

An effective amount of an instant higher alkylbenzotriazole should be used. As used herein, the term "effective amount" refers to that amount of a higher alkylbenzotriazole which effectively inhibits corrosion in a given aqueous system.

More particularly, the higher alkylbenzotriazoles, inhibit the corrosion of metallic surfaces, especially copper and copper alloy surfaces, when added to an aqueous system in contact with such surfaces at a concentration of at least about 0.1 ppm, preferably about 0.5 to 100 ppm and most preferably about 1-10 ppm. Maximum concentrations are determined by the economic considerations of the particular application, while minimum concentrations are determined by operating conditions such as pH, dissolved solids and temperature.

The instant higher alkylbenzotriazoles may be prepared by any known method. For example, the instant alkylbenzotriazoles may be prepared by contacting a 4-alkyl-1, 2-diaminobenzene with an aqueous solution of sodium nitrite in the presence of an acid, e.g., sulfuric acid, and then separating the resultant oily product from the aqueous solution. The 4-alkyl-1,2-diaminobenzene may be obtained from any number of sources.

The instant compounds can be used as water treatment additives for industrial cooling water systems, gas scrubber systems or any water system which is in contact with a metallic surface, particularly surfaces containing copper and/or copper alloys. They can be fed alone or as part of a treatment package which includes, but is not limited to, biocides, scale inhibitors, dispersants, defoamers and other corrosion inhibitors. The instant higher alkylbenzotriazoles can be fed intermittantly or continuously.

Treatment of cooling water which contacts copper or copper alloy surfaces, such as admiralty brass or 90/10 copper-nickel, requires the use of specific copper inhibitors. These inhibitors:

1. minimize the corrosion of the copper or copper alloy surfaces, including general corrosion, dealloying and galvanic corrosion; and
2. minimize problems of galvanic "plating-out" of soluble copper ions onto iron or aluminum. Thus, soluble copper ions can enhance the corrosion of iron and/or aluminum components in contact with aqueous systems. This occurs through the reduction of copper ions by iron or aluminum metal, which is concommitantly oxidized, resulting in the "plating-out" of copper metal onto the iron surface. This chemical reaction not only destroys the iron or aluminum protective film but creates local galvanic cells which can cause pitting corrosion of iron or aluminum.

Conventional copper inhibitors such as tolyltriazole, benzotriazole, and 2-mercaptobenzothiazole are commonly used as copper inhibitors in aqueous systems. They are generally fed continuously because of the limited durability of their protective films.

Continuous feed of an inhibitor generally makes it uneconomical to apply these conventional inhibitors to once-through systems or systems with high blowdown rates. Additionally, conventional inhibitors provide only limited protection against chlorine induced corrosion.

While 5-lower alkylbenzotriazoles are known which do not require continuous feeding in order to inhibit copper corrosion (See U.S. Patent 4,744,950), These compounds provide relatively poor chlorination resistance.

An object of the instant invention is to provide inhibitors which produce more chlorine resistance protective films.

This object is achieved through the use of higher alkylbenzotriazoles, to provide protective, durable hydrophobic films on metallic surfaces, especially copper and copper alloy surfaces.

The instant alkylbenzotriazoles allow use of an intermittent feed to cooling water systems. Depending on water aggressiveness, the time between feedings may range from several days to months. This results in an average lower inhibitor requirement and provides advantages relative to waste treatment and environmental impact.

The preferred alkylbenzotriazoles are within the range of C_6-C_{10} alkylbenzotriazoles. The most preferred compounds are heptylbenzotriazole and octylbenzotriazole.

EXAMPLES

The following examples demonstrate the effectiveness of the instant compounds as copper and copper alloy corrosion inhibitors. They are not, however, intended to limit the scope of the invention in any way.

EXAMPLES 1-5 - FILM PERSISTENCY

In these examples, copper specimens were pretreated by immersing them in aerated water at pH 7.5 and 50°C. This water contained a specified concentration of inhibitor, which formed a protective film on the specimens.

After 24 hours, the specimens were transferred to inhibitor-free water of a highly corrosive nature to determine film persistency. Corrosion rates were measured using linear polarization to determine passivation.

The characteristics of the pretreatment water and the aggressive water are given in Tables I and II, respectively.

Corrosion results are given in Table III. The results are reported as "Corrosion Rates After Passivation" for the passivation step and as "Corrosion Rates In Inhibitor-Free Agressive Water".

TABLE I

Composition of Pretreatment Water	
pH = 7.5	
Ion	Concentration (mg/L)
Ca	260
Mg	115
Cl	476
SO_4	460
SiO_2	9

TABLE II

Composition of Aggressive Water	
pH = 7.5	
Ion	Concentration (mg/L)
Ca	750 as Ca^{+2}
Mg	130 as Mg^{+2}
Cl	2400
SO_4	3200

TABLE III

PASSIVATION AND PERSISTENCY TESTS					
Example	Inhibitor	Concentration (mg/L)	mpy Corrosion Rate After 24 hrs. Pretreatment	mpy Corrosion Rate In Inhibitor-free Aggressive Water	No. of days In Inhibitor-free Aggressive Water
1*	None	0	1.1	2.5-3.0	15
2*	Tolyltriazole	5	0.01	5-6	1
3*	Butylbenzotriazole	5	0.005	0.2	15
4	Heptylbenzotriazole	5	0.005	< 0.005	15
5	Octylbenzotriazole	5	0.005	< 0.005	15

* Comparison Examples

Table III shows that heptylbenzotriazole and oxtyloxybenzotriazole provided 99% inhibition, even after 15 days exposure to aggressive water, and that tolyltriazole, a conventional inhibitor, failed within one day. This is surprising in view of the teachings of U.S. Patent No. 4,744,950.

Examples 6-9 - Chlorine Chemical Resistance

In these examples, copper specimens were pretreated by immersing them in aerated water at pH 7.5 and 50°C. This water contained a specified concentration of inhibitor, which formed a protective film on the specimens.

After 24 hours, the specimens were transferred to inhibitor-free water of the same composition as the pretreatment water. Chlorine was added so that a initial free residual of 1 mg/L chlorine was obtained. Corrosion rates were measured using linear polarization over the course of one hour. The probes were then transferred to fresh inhibitor-free, chlorine-free water and the corrosion rate was monitored to determine the recovery corrosion rate.

This chlorination procedure was repeated 8 times on a daily basis, plus an additional time after the weekend period.

The water composition is given in Table IV.

TABLE IV

WATER COMPOSITION USED IN THE CHLORINE CHEMICAL RESISTANCE EXAMPLES 6-9	
Ion	Concentration (mg/L)
Ca	88
Mg	24
Cl	70
SO_4	325
pH	7.5

The results are given in Table V. The copper specimens treated with heptylbenzotriazole and octylbenzotriazole were practically immune to the aggressiveness of chlorine. In contrast, the butylbenzotriazole treated specimen showed progressively less corrosion protection in the presence of chlorine, and gave progressively higher recovery corrosion rates after each chlorination.

In further contrast, tolyltriazole treated specimens gave higher corrosion rates in the presence of chlorine and unacceptably high recovery corrosion rates following chlorination.

EXAMPLES 10-13 - Chlorine Resistance

These examples, which were run in a dynamic test unit, demonstrate the resistance of protective films formed by heptylbenzotriazoles to corrosiveness caused by chlorine on heat-transfer brass tubes and on immersed copper coupons.

The dynamic test unit for these examples consisted of an 8L reservoir, a heater-circulator and a coil heater to provide the desired heat flux. The coil heater was designed to fit securely around the 3/8" OD tubes used in the tests. Flow through the tube was monitored by an in-line rotameter having a flow capacity of 400 ml/min. The power input to the heater was controlled by a rheostat, which made it possible to vary temperature differences across the tubes. The tube inlet and outlet temperatures were monitored by thermocouples attached to a digital readout having an accuracy of 0.1°F. The system was entirely enclosed to minimize evaporation. The linear velocity through the heated tubes was 2.2 fps, which gave a N_{Re} of approximately 9350. Heat fluxes of 8,000-10,000 Btu/hr-ft^2 were chosen as being representative of industrial practices.

The corrosion rates of the heated tubes were determined by the weight loss method described in "Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens"; ASTM designation GI-81. The corrosion rates of immersed specimens were determined by linear-polarization using a Petrolite Model M1010 Corrosion Data Acquisition System. This method measures the corrosion rate at a particular time, and is thus useful for following the immediate effects of chlorine concentration on corrosion rates.

The following procedure was followed relative to the test specimens:

1. Cleaned specimens were placed in the test unit described above, and a specified amount of inhibitor was added.

The specimens were then allowed to passivate for 24 hours at which time they were placed in inhibitor-free water.

2. Chlorine was added to give an initial concentration of 1 mg/L free chlorine. The corrosion rate of each specimen was monitored for one hour. The chlorine concentration normally decreased from 1 mg/L to about 0.7 mg/L during this time.

3. After one hour, each specimen was placed in fresh inhibitor-free, chlorine-free water. The decrease in corrosion rate, i.e. the recovery corrosion rate, was then measured for each specimen.

4. Steps 2 and 3 were repeated in 24 hour cycles for a total of four cycles, with one additional cycle following a weekend period.

5. After a seven day period, the weight loss of the heated tube was determined.

The composition of the water used in these tests is given in Table VI.

The results are shown in Table VII. The corrosion rates of the heat-transfer Admiralty brass tubes show the cumulative corrosion which occurred during the 7-day test period. As can be seen, heptylbenzotriazole gave over 85 percent corrosion protection while butylbenzotriazole gave the same corrosion protection. This is surprising in view of the teachings of Holander U.S.#4,744,950.

TABLE V

Chlorine Chemical Resistance													
Example	Inhibitor	Pretreatment Concentration (mg/L)	Conc. Rate after 24 Hours Pretreatment	Maximum Conc. Rate during Chlorination (mpy)					Recovery Corrosion Rates after 18 Hours (mpy)				
				1st	2nd	3rd	4th	5th	1st	2nd	3rd	4th	5th
6	Butylbenzotriazole	5	0.005	0.5	0.8	1.6	2.0	3.7	0.01	0.01	0.01	0.08	0.14
7	Totyltriazole	5	0.005	4.5	4.5	-	-	-	0.2	0.7	-	-	-
8	Octylbenzotriazole	5	< 0.005	0.01	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
9	Heptylbenzotriazole	5	< 0.005	0.01	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

TABLE VI

COMPOSITION OF WATER USED FOR EXAMPLES 10-13	
Ion	Concentration (mg/L)
Ca	260
Mg	115
Cl	476
SO_4	460
SiO_2	9
pH	7.5

TABLE VII

EFFECT OF CHLORINATION ON CORROSION RATES OF HEAT-TRANSFER ADMIRALTY BRASS TUBES AND IMMERSED COPPER PROBES

Ex. No.	Inhibitor	Conc. mg/L	Admiralty Brass Tubes (by wt. loss)	% CP*	Copper-Probes Max. Corrosion Rates during Cl_2 Contact during The Last Chlorination	Recovery Corrosion Rate 18 hr. after Cl_2 Removal
10	None	0	3.4		5	1.5
11	Heptyl BT	10	0.5	86	0.01	< 0.01
12	Butyl BT	5	0.5	86	0.03	0.01
13	Tolyltriazole	5	2.2	36	2	1.0

$$* \% CP = \frac{\text{blank - inhibited}}{\text{blank}} \times 100\%$$

Also, tolyltriazole, which is a widely used inhibitor, gave only 36 percent corrosion protection. Also, the immersed copper probes treated with heptylbenzotriazole was not significantly affected by exposure to chlorine over the 1 hour contact time while the copper probes treated with tolyltriazole and the untreated probes experienced dramatically higher corrosion rates in the presence of chlorine.

EXAMPLES 14 - 16 - Film Persistency

The experimental procedure of Examples 17-19 was used. However, no chlorine was added to the system. The purpose of this test was to determine the persistency of the protective film formed by the inhibitor after the inhibitor had been exhausted from the system due to replacement of the original water.

The results are shown in Table VIII, which shows that heptylbenzotriazole provided durable protection throughout the two (2) week test. This is especially surprising in view of the practically complete depletion of original inhibitor concentration by the fifth day. The test was terminated after two (2) weeks only due to practical limitations of time and expense.

EXAMPLES 17-19 - Dynamic Pilot Cooling Tower Tests

These examples illustrate the outstanding chlorine resistance and film persistency of heptylbenzotriazole in a dynamic system which simulates the operational variations commonly found in industrial cooling towers. Operational factors simulated include blow-down, heat transfer surfaces, dynamic flow, evaporative-cooling, cycles of concentration, and customary chlorination practices.

The pilot cooling tower system used contained two single tube heat exchangers. Cooling water flowed in series through the shell side (annular space) of the heat exchangers and hot water was circulated through the tubes in series, counterflow. In addition to the main recirculation circuit through the cooling tower, the system also contained a recycle loop from the outlet of the No. 2 Heat Exchanger to the inlet of the No. 1 Heat Exchanger for the purpose of maintaining cooling water linear velocity in the heat exchangers. The heat exchanger shells were fabricated of Plexiglass to permit observation of the heat exchanger surfaces during the test run. For these tests, a 90/10 copper/nickel tube was placed in the No. 2 Heat Exchanger.

Instrumentation for monitoring and control of test variables included a pH and conductivity indicator/controller, PAIR corrosion rate indicators, a temperature indicator/controller, and rotometers for air and water flows.

PAIR probes for continuous monitoring of 90/10 copper/nickel corrosion rates were installed after the outlet of the No. 2 Heat Exchanger. A corrosion test coupon of 90/10 copper/nickel was installed in the recycle loop. The PAIR cells and the corrosion test loop were fabricated of Plexiglass to permit observation of the Corrater electrodes and the corrosion coupons.

The cleaning procedures employed to prepare tubes, corrosion coupons and PAIR electrodes for use in these tests are described in ASTM standard GI-81.

In preparation for these tests, stainless steel tubes were installed in the heat exchangers and the system was filled with makeup water. The system required three days for the recirculating water to concentrate to the target cycles of concentration. The target water composition was the same for Examples 10-13. After the target cycles were reached, the stainless steel tubes were removed and the test specimens installed (tubes, coupons, and PAIR electrodes). At this time, blowdown commenced and the desired copper inhibitor was added.

The results are shown in Table IX. The inhibitor was allowed to deplete by gradually replacing the cooling water. Thus, after three (3) days, less than one-eighth of the original inhibitor concentration was present, and after five (5) days, practically no inhibitor remained. Table IX shows the corrosion rate just prior to the addition of chlorine to the system and the maximum corrosion rate recorded while chlorine was present. Chlorine was added so that between 0.2 mg/L to 0.5 mg/L free residual of chlorine was present. The chlorine concentration was then allowed to dissipate through blow-down, evaporation, and reaction.

As can be seen in Table IX, heptylbenzotriazole effectively passivated the 90/10 copper/nickel specimens and dramatically reduced the aggressiveness of chlorine even, surprisingly, when all of the inhibitor had depleted. In contrast, butylbenzotriazole afforded only minimal protection against attack by chlorine, as seen by both the deteriorating recovery corrosion rate and the large corrosion rate experienced during the chlorination.

This is surprising especially in view of the teachings of Holander, USP 4,744,950.

TABLE VIII

INHIBITION PERSISTENCY OF HEXYLBENZOTRIAZOLE IN THE PILOT COOLING TOWER

Day	Example 14 Blank (no inhibitor)	Example 15 Heptylbenzotriazole 5 mg/L Initial Charge	Example 16 Butylbenzotriazole 5 mg/L Initial Charge
0	13	4.5	8
1	5	0.07	0.25
2	3.5	0.05	0.2
3	2.5	0.03	0.2
4	2.5	0.03	0.15
5	2.5	0.02	0.15
6	2.0	0.02	0.15
7	2.0	0.03	0.2
8	2.0	0.02	0.15
9	2.0	0.03	0.2
10	2.0	0.03	0.15*
11	1.8	0.03	0.15
12	2.0	0.03	0.20
13	1.5	0.03	0.25
14	1.4	0.03	0.25

* a pH excursion to pH 5 occurred on the 10th day, the pH was corrected by the next day.

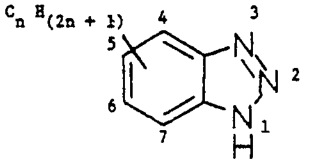
TABLE IX

Pilot Cooling Tower Test with Chlorination: Effectiveness of Heptylbenzotriazole							
Corrosion Rates (mpy) on Cu/Ni 90/10							
	EXAMPLE 17		EXAMPLE 18			EXAMPLE 19	
	Control (No Inhibitor)		5 mg/L Heptylbenzotriazole Initial Charge			5 mg/L Butylbenzotriazole Initial Charge	
Day	Rate Prior to Chlorination	Max. Rate In Presence of Cl_2	Rate Prior to Chlorination	Max. Rate In Presence of Cl_2	Day	Rate Prior to Chlorination	Max. Rate In Presence of Cl_2
1	2.0	No Cl_2 Added	0.005	No Cl_2 Added	1	0.1	-
2	2.0	No Cl_2 Added	0.005	No Cl_2 Added	2*	0.1	-
3*	1.5	7.8	0.005	0.005	3*	0.1	0.4
4*	0.9	5.8	0.005	0.005	4*	0.2	2.6
5*	0.7	2.8	0.005	0.005	5*	0.3	1.8
6*	0.5	2.3	0.005	0.005	6*	0.5	4.5
7*	0.7	1.7	0.005	0.005	7*	1.0	4.5
	Tube appearance uniformly darkened after Day 7		Bright, very slight tarnish				

* Chlorine was added to the system on the indicated days.

Claims

1. A method of inhibiting corrosion in an aqueous system which is in contact with a metallic surface, comprising adding to said system an effective amount of a compound selected from the group of compounds having the following formula:



wherein n is greater than 6 and less than equal to 12.

2. The method of Claim 1, wherein about 0.1 to about 10.0 mg/l of said compound is added to said aqueous system.

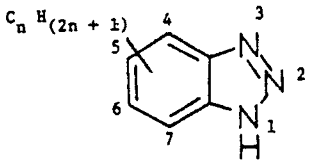
3. The method of Claim 1, wherein said compound is selected from the group consisting of heptylbenzotriazole and octylbenzotriazole.

4. The method of Claim 2, wherein said compound is selected from the group consisting of heptylbenzotriazole and octylbenzotriazole.

5. The method of Claim 1, wherein said metallic surface is a copper or copper alloy surface.

6. The method of Claim 2, wherein said surface is a copper or copper alloy surface.

7. A composition comprising: a) the water of an aqueous system; and b) compounds selected from the group of compounds having the following formula:



wherein n is greater than 6 and less than or equal to 12.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 4952

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 173 427 (BETZ EUROPE INC.) * Claims 1,2,7,9,10 * ---	1-7	C 23 F 11/14
X	GB-A-1 065 995 (GEIGY LTD) * Claims 1,4,15; page 2, lines 46-53 * ---	1,5,7	
X	FR-A-2 114 466 (CIBA GEIGY) * Claims 1,2,7,8 * ---	1,3,5,7	
A	DE-A-2 155 766 (CIBA GEIGY AG) ---		
D,A	EP-A-0 258 021 (BETZ EUROPE INC.) ---		
A	CH-A- 439 546 (J.R. GEIGY AG) ---		
A	PATENT ABSTRACTS OF JAPAN, vol. 6, no. 261 (C-141)[1139], 21st December 1982; & JP-A-57 152 476 (CHIYODA KAGAKU KENKYUSHO K.K.) 20-09-1982 -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 23 F 11/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25-07-1990	TORFS F.M.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)