(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 555 006 A1**

# (12) EUROPEAN PATENT APPLICATION

(21) Application number : **93300598.5**

(22) Date of filing : **27.01.93**

(51) Int. Cl.$^5$ : **C10L 1/22,** C10L 1/18

(30) Priority : **07.02.92 CS 351/92**

(43) Date of publication of application :
**11.08.93 Bulletin 93/32**

(84) Designated Contracting States :
**AT ES FR GB IT**

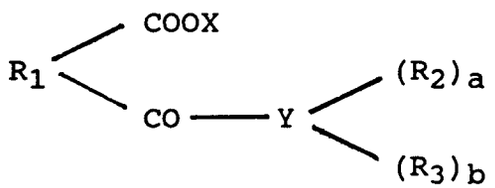
(71) Applicant : **SLOVNAFT A.S.**
**Vicie hrdlo**
**CS-824 12 Bratislava, Slovak Republic (CS)**

(72) Inventor : **Oravkin, Juraj**
**Rovniankova 4**
**CS-851 02 Bratislava, Slovak Republic (CS)**
Inventor : **Bratsky, Daniel**
**Szantova 73**
**CS-841 03 Bratislava, Slovak Republic (CS)**
Inventor : **Feher, Pavol**
**Dunaksla 4**
**CS-931 01 Samorin, Slovak Republic (CS)**
Inventor : **Boska, Milos**
**Martincekova 3**
**CS-821 09 Bratislava, Slovak Republic (CS)**

(74) Representative : **Enskat, Michael Antony Frank**
**Saunders & Dolleymore 9, Rickmansworth Road**
**Watford Hertfordshire WD1 7HE (GB)**

## (54) Derivatives of dicarboxylic acids as additives in unleaded automobile gasolines.

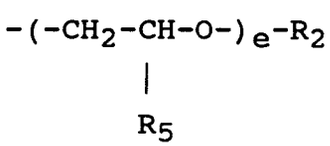
(57) The derivatives have a structural chemical formula I



(I)

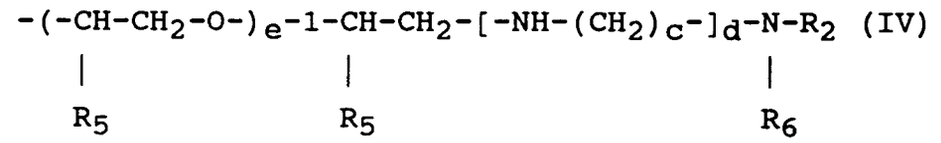
where
$R_1$
is a bivalent hydrocarbon functional group or hydrocarbon functional group with nitrogen atoms in amino-position and/or etheric position with total number of carbon atoms from 1 to 38,
R2
is a monovalent hydrocarbon functional group with a number of carbon atoms from 1 to 42 or hydrogen,
X
is a hydrogen and/or alkaline metal and/or alkaline earth metal,
Y
is oxygen or nitrogen,
a and b
are cardinal numbers zero or 1, selected such that $a + b \geqq 1$,
$R_3$
is hydrogen or a monovalent hydroxy-substituted hydrocarbon functional group with a number of carbon atoms from 1 to 42 or a monovalent hydrocarbon functional group with a number of carbon atoms from 1 to 42 or a monovalent functional group of structural chemical formula II or III or IV,

$$-[-(CH_2)_c-NH-]_dR_4 \qquad (II)$$

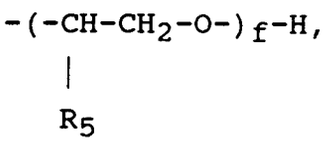


(III)

EP 0 555 006 A1



where
$R_4$
is hydrogen or a monovalent hydrocarbon functional group with a number of carbon atoms from 1 to 42 or a functional group of structural chemical formula III,
$R_5$
is hydrogen or a monovalent hydrocarbon functional group having a number of carbon atoms from 1 to 3,
$R_5$
is hydrogen or a functional group



c
is a cardinal number from 1 to 10,
d
is a cardinal number from zero to 6,
e
is a cardinal number from 1 to 50,
f
is a cardinal number from 1 to 50.

The invention relates to derivatives of dicarboxylic acids as additives in low-leaded or unleaded automobile gasoline that minimize wear of exhaust valve seats in automobile engines that are not designed for internal combustion of unleaded automobile gasoline.

The tendency to go over to the use of unleaded automobile gasoline is apparent in the whole world as a result of the effort to have healthier environment. Production of unleaded automobile gasoline was started in the USA at the beginning of the 1970s, in Japan in 1974 and in Europe at the beginning of 1984. Since then its share on gasoline production and consumption is rapidly increasing. The tendency in the whole world is to produce and use only unleaded automobile gasoline. For example, only unleaded gasoline has been used in Japan since March 1986. In the USA its share on the total production was more than 90 % in 1990 and full suspension of leaded gasoline production is considered for the beginning of the 1990s. In Europe, considering certain shift and difference in the automobile park and in technical possibilities of refineries, the situation is not so unambiguous as overseas. Unleaded gasoline seeks its market place in every country at a different rate.

In the advanced countries of Europe the share of unleaded gasoline production on the total gasoline production is about 50 % at present. The share of unleaded gasoline on the total gasoline production is estimated to be at least 75 % by 1995 in comparison with 21.3 % in 1986 and 26 % in 1987. In Czechoslovakia unleaded gasoline has been produced and sold since 1986. In 1990 the share of its production on the total gasoline production did not exceed 3 %.

The production and distribution of unleaded automobile gasoline encounter a big problem which, together with technical capabilities of refineries, is the main obstacle to instant change over to the production and use of unleaded fuel, namely the fact that it is impossible to use unleaded gasoline in automobile engines designed for leaded fuel. Use of unleaded gasoline in such automobile engines results in damage to the cylinder head or to the whole engine and the automobile becomes unusable. It is essentially both an old and a new problem encountered by automobile producers already at the beginning of the 1920s which was "solved by itself" when lead-based antiknocking agents were added to gasolines. The number of automobiles in the world that could be damaged by the use of unleaded automobile gasolines was estimated to be 70 million in 1987, of it about 7 million in the UK. In Czechoslovakia the number of automobiles that cannot use unleaded fuel is estimated to be approximately 70 % of the total number of passenger vehicles and considering the statistically determined 5 % replacement of passenger automobiles in Czechoslovakia annually, their total disappearance is expected not sooner than by 2010.

Nearly all automobiles produced before 1972 belong to this group. On the other hand since 1986 most car producing factories have been producing models that can use unleaded gasolines.

The reason why an engine is damaged if unleaded fuel is used is the quality of the material used in the production of exhaust valve seats and of the whole cylinder head of the engine. If such parts are made of cast iron or similar "soft" material, they are rapidly abraded and worn off. As a consequence of this, exhaust valves gradually recede into the cylinder head and the valve clearance becomes gradually smaller. The final stage of this process is imperfect closing of the combustion space, loss of compression and engine power, burning of exhaust valves and their seats. In the end the engine cylinder head is damaged beyond repair.

In reality, only towards the close of the use of lead in automobile gasoline it has been shown that apart from increasing the antiknocking stability lead fulfilled another very important function in gasoline that consisted in the protection of exhaust valve seats against mechanical wear engine operation. It is supposed that combustion products of lead-based antiknocking agents form a thin protective film on the surface of valve seats that prevents high-temperature oxidation and wear and lowering adherence and transfer of material thereby protecting the seats against unwanted wear [Automotive Engineering, 95, 11, 72 1987].

Possible solutions to the mentioned problem that would make use of unleaded fuel possible also in this group of automobiles may be one of the following:

(a) Replacement of the cylinder head of such automobiles by a head having specially hardened exhaust valve seats. This is in reality impossible for many running-out car makes and is also financially unacceptable to users.

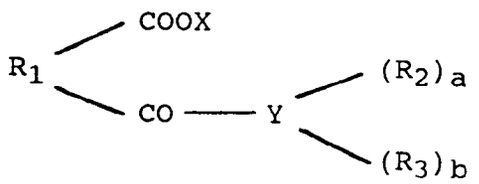
(b) Addition of such additive to the unleaded automobile gasoline that is harmless to health and catalytic convertors and replaces the film-forming function of lead compounds giving the necessary protection to exhaust valve seats. In the world market only two additives for such purpose are available at present. They were relatively effective in a number of foreign engines but they were not able to provide effective protection to ŠKODA engines against exhaust valve seat recession even if they were added at doses several times higher than those recommended by the producer [Bratsky, D, Freher, P Oravkin, J, Malach, V : Development Trend in the Field of Automobile Gasolines and their Additives, Study of VURUP, Bratislava, 1990].

Another possibility is to use leaded gasoline for as long as such automobile engines will be in operation.

However, in this case production of leaded gasoline cannot be terminated with resulting consequences to the environment.

The most suitable solution to this situation is to use only unleaded automobile gasolines that contain derivatives of dicarboxylic acids according to this invention. Their addition guarantees that in combustion of unleaded or low-leaded automobile gasolines seats of exhaust valves produced from non-hardened materials, e.g. from cast iron, are not damaged. Additives based on derivatives of dicarboxylic acids described in this specification are harmless to health and do not deteriorate catalytic convertors of exhaust gases.

Derivatives of dicarboxylic acids according to this invention have structural chemical formula I:



(I)

where

$R_1$ is a bivalent hydrocarbon functional group or hydrocarbon functional group with nitrogen atoms in amino-position and/or etheric position with total number of carbon atoms from 1 to 38,

$R_2$ is a monovalent hydrocarbon functional group with a number of carbon atoms from 1 to 42 or hydrogen,

X is hydrogen and/or alkaline metal and/or alkaline earth metal,

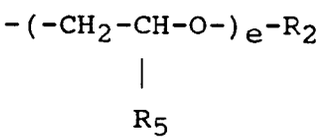
Y is oxygen or nitrogen,

a and b are cardinal numbers zero or 1, selected such that $a + b \geqq 1$,

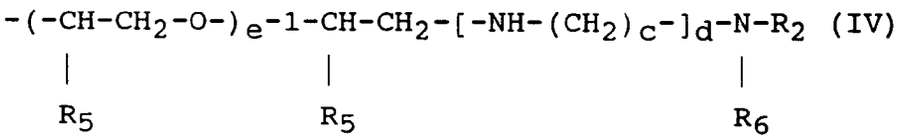
$R_3$ is hydrogen or a monovalent hydroxy-substituted hydrocarbon functional group with a number of carbon atoms from 1 to 42 or a monovalent hydrocarbon functional group with a number of carbon atoms from 1 to 42 or a monovalent functional group of structural chemical formula II or III or IV,



(II)



(III)



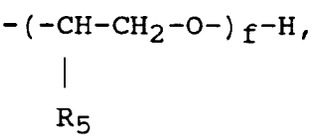
(IV)

where

$R_4$ is hydrogen or a monovalent hydrocarbon functional group with a number of carbon atoms from 1 to 42 or a functional group of structural chemical formula III,

$R_5$ is hydrogen or a monovalent hydrocarbon functional group having a number of carbon atoms from 1 to 3,

$R_5$ is hydrogen or a functional group



c is a cardinal number from 1 to 10,

d is a cardinal number from zero to 6,

e is a cardinal number from 1 to 50,

f is a cardinal number from 1 to 50.

Such derivatives of dicarboxylic acids if added to unleaded automobile gasolines are effective inhibitors of exhaust valve seats wear in car engines that are not designed for the combustion of unleaded automobile gasoline and make their permanent trouble-free operation with this fuel possible.

To improve manipulation, especially viscosity and thereby also pumpability in the stage of filling into packages, transport and application, the derivatives of dicarboxylic acids as additives to automobile gasolines according to this invention can contain also an auxiliary component, such as an organic solvent, preferably of aromatic type. Suitable solvents are toluene, xylene, aromatic hydrocarbons with 9 to 13 carbon atoms in molecule or their technical blends, eg reformate of heavy gasoline, fractions from reformate having boiling point in the range from 75 °C to 250 °C, fractions from pyrolysis gasoline with a similar distillation range. Aromatic hydrocarbons content in such blends is usually above 25 % wt.

To guarantee the above mentioned effects of additives based on dicarboxylic acids according to the invention they are added to automobile gasoline in concentration from 0.025 wt. to 1.1 % wt. If the additive according to the invention contains an auxiliary component which is the above specified organic solvent, the amount of this blend is so selected that the concentration of the effective component is in the above specified range.

To improve the pumpability and also to keep its required content in the automobile gasoline, it is possible to further dilute the additive according to this invention by the addition of automobile gasoline, some of its components or by other hydrocarbon solvent, before it is added to gasoline.

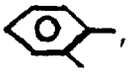
The additive according to this invention can be added to gasoline either directly at the stage of automobile gasoline preparation in a refinery (primary addition) or it is possible to add this additive to the finalized gasoline at the stage of its consumption or distribution, e.g. in filling stations (secondary addition). The secondary addition of this additive according to this invention is preferable especially in such cases when automobile gasoline is produced without its content.

The following examples illustrate the advantages and practical use of the specified dicarboxylic acids according to the invention as additives in automobile gasolines, however, without limiting the subject of this invention in any way.

Example 1

A four-cylinder spark-ignition engine ŠKODA with a cylinder capacity 1174 $cm^3$ having cast iron cylinder head was tested by a stationary engine test under conditions specified in Table 1. Unleaded gasoline (0.000 g Pb/l) having RON (research method) 96 octanes and MON (motor method) 87 as well as low-leaded automobile gasoline containing 0.013 g Pb/l having the same RON and MON were tested. During the test valve clearance was measured every 6 hours and when necessary valve clearance was adjusted so that the minimum value was never lower than 0.2 mm. At the end of the 36 h engine test the cylinder head of the engine was dismantled and the suction and exhaust valves removed. Change of valve weight was determined and total recession of exhaust valve seats was measured. Results obtained are listed in Tables 2 and 3. Individual values represent both average recession for four cylinders and the value for one cylinder with the deepest recession. Results of the test have shown that use of unleaded automobile gasoline in the engines of this type is not possible.

A similar test was carried out also with unleaded automobile gasoline (0.0000 g Pb/l) that contained 850 ppm of the derivative of dicarboxylic acid according to the invention with structural chemical formula (I), where $R_1$ is

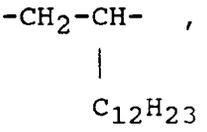
 ,

X is $Ca^{2+/2}$, Z is nitrogen, $R_2$ is hydrogen, a = 1, b = 1, $R_3$ is $-[-CH_2)_c-NH-]_d-R_4$, where c = 2, d = 2 and $R_4$ is polypropenyl- of average molecular weight 450 g/mol.

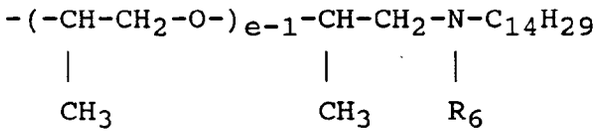
The mentioned derivative of dicarboxylic acid was prepared by reaction of phthalic anhydride with N-polypropenyl-diethylene-triamine and subsequent neutralization of the formed derivative of the phthalamic acid by calcium oxide. Results of this test have shown that there has not been observed any recession of exhaust valve seat by any valve and this was the case even when the test was prolonged to 56 hours. Average change of the exhaust valve clearance was -0.0075 mm, the maximum determined value was -0.04 mm.

Example 2

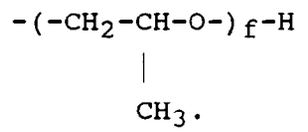
A long time (300) life expectancy stationary engine test was carried out with a four-cylinder spark-ignition engine ŠKODA S 742.13 having a cast iron cylinder head under conditions according to Czechoslovak standard CSN 30 0506. Unleaded gasoline having octane number RON 96 and MON 87 (0.004 g Pb/l) was used. The used fuel was modified by 700 ppm of an additive according to this invention having the structural chemical formula (I), where $R_1$ is



X is sodium, Z is oxygen and a is zero, b is 1, $R_3$ is



where e is 3 to 5
and $R_6$ is



where f is 1 to 3.

The specified derivative of the dicarboxylic acid was prepared by reaction or tetrapropenylsuccin anhydride with propoxylated tetradecylamine and subsequent neutralization of the produced semiproduct by sodium hydroxide.

Additive of this composition was dissolved in reformate of heavy gasoline before addition to unleaded automobile gasoline for easier handling so that the effective solution contained 50 % of the effective component.

Results of this test have shown that no exhaust valve recession was observed in any engine cylinder. The average change of exhaust valve clearance was 0.055 mm. Unleaded automobile gasoline containing the above mentioned additive according to this invention fully protected exhaust valve seats of the engine. No deterioration of operational characteristics was observed and engine life expectancy was maintained.

Example 3

The automobile park presented in table 4 was used to carry out road engine tests of 50,000 km to 80,000 km. New engines, carburetters, fuel tanks and suction pipelines were used in the automobiles. Unleaded automobile gasoline (0.001 to 0.005 g Pb/l) was used having octane number RON 95 to 97 containing 7 to 12 % vol of methyl tert. butyl ether (MTBE) modified by 750 ppm of the derivative of dicarboxylic acid according to this invention having structural chemical formula (I) where $R_1$ is -CH=CH-, X is sodium, Z is nitrogen, $R_2$ is phenyl-, a is 1, b is 1, R is $C_{12}H_{25}$-.

The specified derivative of the dicarboxylic acid was prepared by reaction of the corresponding secondary amine with maleic anhydride and by subsequent neutralization of the formed semiproduct by sodium hydroxide.

Before addition of the above additive to the unleaded automobile gasoline the additive of this composition was dissolved in an aromatic solvent having boiling point between 140 and 190°C to make its handling easier so that the resulting solution contained 10 % of the effective component.

During the tests all vehicles were used predominantly in city and highway traffic. After every 5,000 km exhaust valve clearance was checked, after 10,000 km power and emission characteristics of the vehicles were

checked as well as fuel consumption and octane requirement. In case of vehicles with catalyst, catalyst efficiency was determined. After the end the tests the engines were dismantled and completely evaluated.

The evaluation has shown that the additive according to the invention provides perfect protection to exhaust valve seats in all automobiles tested to their wear during combustion of unleaded gasoline. The additive has negative influence on any function of a spark-ignition engine and on its life expectancy. This additive is harmless to catalytic systems for exhaust gas purification and does not deteriorate emissions of spark-ignited engine.

Table 1

Conditions of the Stationary Engine Test

| Composition of the Test Cycle | | | |
|---|---|---|---|
| Stage | Duration [min] | Engine Speed [1. $min^{-1}$] | Engine Load |
| 1st | 20 | 3000 | full |
| 2nd | 10 | 850 | idle running |
| 3rd | 20 | 5000 | full |
| 4th | 10 | 850 | idle running |

Table 2

Influence of the test time on exhaust valve recession if unleaded gasoline (0.000 g Pb/l) not containing the additive according to the invention was used.

| Number of hours | Recession of Exhaust average for 4 cylinders | Valve Seats [mm] max. of one cylinder |
|---|---|---|
| 12 | 0.26 | 0.35 |
| 24 | 0.45 | 0.60 |
| 36 | 0.80 | 1.19 |

Table 3

Influence of the test time on exhaust valve recession if leaded gasoline (0.013 g Pb/l) not containing the additive according to the invention was used

| Number of hours | Recession of Exhaust Valve Seats [mm] | |
|---|---|---|
| | average for 4 cylinders | max. of one cylinder |
| 12 | 0.12 | 0.23 |
| 24 | 0.32 | 0.54 |
| 36 | 0.43 | 0.76 |

Table 4

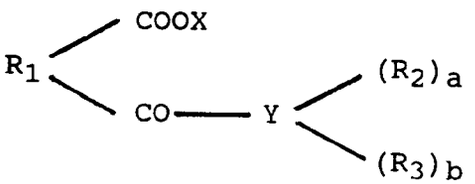
Automobile Park Used in the Road Engine Tests

| Vehicle Type | Number of Vehicles |
|---|---|
| ŠKODA 120 L | 3 |
| ŠKODA 130 L | 8 |
| ŠKODA FAVORIT 136 L with catalyst | 4 |
| VOLGA GAY 24.10 | 2 |
| OLTCIT 11 R | 3 |

Application of the derivatives of the dicarboxylic acids according to the invention in unleaded automobile gasoline enables permanent operation of all automobiles with spark-ignition engines with this environmentally preferred fuel so that instant transfer from leaded automobile gasoline to the sole production and use of unleaded fuel is possible.

## Claims

1. Derivatives of dicarboxylic acids as additives in low-leaded or unleaded automobile gasoline that minimize wear of exhaust valve seats in automobiles not designed for the use of unleaded automobile gasoline, which have a structural chemical formula I.



(I)

where

$R_1$ is a bivalent hydrocarbon functional group or hydrocarbon functional group with nitrogen atoms in amino-position and/or etheric position with total number of carbon atoms from 1 to 38,

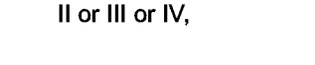
$R_2$ is a monovalent hydrocarbon functional group with a number of carbon atoms from 1 to 42 or hydrogen,

X is a hydrogen and/or alkaline metal and/or alkaline earth metal,

Y is oxygen or nitrogen,

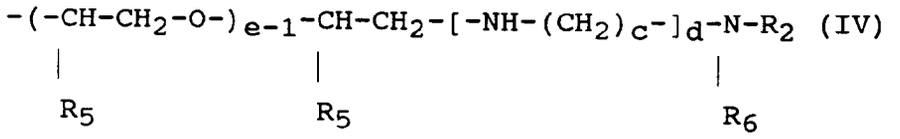
a and b are cardinal numbers zero or 1, selected such that $a + b \geqq 1$,

$R_3$ is hydrogen or a monovalent hydroxy-substituted hydrocarbon functional group with a number of carbon atoms from 1 to 42 or a monovalent hydrocarbon functional group with a number of carbon atoms from 1 to 42 or a monovalent functional group of structural chemical formula II or III or IV,



(II)

(III)

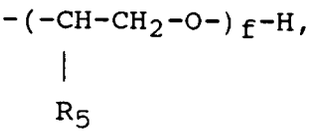


where

$R_4$ is hydrogen or a monovalent hydrocarbon functional group with a number of carbon atoms from 1 to 42 or a functional group of structural chemical formula III,

$R_5$ is hydrogen or a monovalent hydrocarbon functional group having a number of carbon atoms from 1 to 3,

$R_6$ is hydrogen or a functional group



c is a cardinal number from 1 to 10,

d is a cardinal number from zero to 6,

e is a cardinal number from 1 to 50,

f is a cardinal number from 1 to 50.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 93 30 0598

## 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-0 301 448 (BASF)<br>* page 6, line 32 *<br>* page 7, line 16 - line 17 * | 1 | C10L1/22<br>C10L1/18 |
| P,X | EP-A-0 491 439 (SHELL)<br>* page 4, line 5 * | 1 | |
| X | US-A-2 433 716 (SMITH ET AL.)<br>* the whole document * | 1 | |
| X | US-A-3 264 075 (GEE ET AL.)<br>* the whole document * | 1 | |
| X | US-A-2 699 427 (SMITH ET AL.)<br>* the whole document * | 1 | |
| X | US-A-4 304 690 (SCHULZE ET AL.)<br>* examples 2,3 * | 1 | |
| X | US-A-3 905 781 (DORN)<br>* the whole document * | 1 | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| X | US-A-4 144 035 (MOSS ET AL.)<br>* the whole document * | 1 | C10L |
| X | US-A-3 088 815 (HANEY ET AL.)<br>* the whole document * | 1 | |
| X | US-A-3 485 858 (GEE ET AL.)<br>* the whole document * | 1 | |
| X | US-A-2 993 773 (STROMBERG)<br>* column 8, line 64 - line 75 * | 1 | |
| X | US-A-2 993 771 (STROMBERG)<br>* column 25, line 58 - line 75 * | 1 | |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 02 JUNE 1993 | DE LA MORINERIE |

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)