(CONVENTION. By one or more persons and/or a Company.) 637459 Form 4.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address(es).

~~We~~/Our(1) HOECHST AKTIENGESELLSCHAFT,
D-6230 Frankfurt am Main 80,
Federal Republic of Germany

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled:(2)
HIGHLY CONCENTRATED EMULSIFIABLE CONCENTRATES OF NEOPHANES AND AZANEOPHANES FOR USE IN PLANT PROTECTION

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered(3)

(3) Here insert number(s) of basic application(s).

P 40 05 153.6

(4) Here insert Name of basic Country or Countries, and basic date or dates.

for a patent or similar protection made in(4) Federal Republic of Germany on 17th February, 1990

~~My~~/Our address for service is WATERMARK PATENT & TRADEMARK ATTORNEYS 290 Burwood Road, Hawthorn, Victoria, Australia.

DATED this 14th day of February, 19 91

(5) Signature(s) of Applicant(s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

(5) HOECHST AKTIENGESELLSCHAFT

By: D.B. MISCHLEWSKI

Registered Patent Attorney

To: THE COMMISSIONER OF PATENTS.

901F053

COMMONWEALTH OF AUSTRALIA - Patents Act 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION UNDER PART XVI., FOR A PATENT

In support of the Convention application made under Part XVI. of the Patents Act 1952 by HOECHST AKTIENGESELLSCHAFT D-6230 Frankfurt am Main 80, Federal Republic of Germany

for a patent for an invention entitled:

Highly concentrated emulsifiable concentrates of neophanes and azaneophanes for use in plant protection

I/We, Martin Fenske, Am Wiesenhof 10, D-6242 Kronberg im Taunus
Franz Lapice, Sandweg 2, D-6233 Kelkheim (Taunus) / Fed.Rep. of Germany

do solemnly and sincerely declare as follows:

1. We are authorized by HOECHST AKTIENGESELLSCHAFT the applicant/~~s~~ for the patent to make this declaration on its/~~their~~ behalf.

2. The basic application/~~s~~ as defined by Section 141 of the Act was/~~were~~ made by HOECHST AKTIENGESELLSCHAFT
Federal Republic of Germany P 40 05 153.6 of February 17, 1990

3.

Hans RÖCHLING, Geierfeld 25, D-6232 Bad Soden im Taunus
Fed.Rep.of Germany

is/~~are~~ the actual inventor/~~s~~ of the invention and the facts upon which HOECHST AKTIENGESELLSCHAFT is/~~are~~ entitled to make the application are as follows:
The said HOECHST AKTIENGESELLSCHAFT
is/~~are~~ the assignee/~~s~~ of the said inventor/~~s~~

4. The basic application/~~s~~ referred to in paragraph 2 of this Declaration was/~~were~~ the the first application/~~s~~ made in a Convention country in respect of the invention the subject of the application.

Dated Frankfurt am Main, Fed.Rep.of Germany, January 29, 1991

HOECHST AKTIENGESELLSCHAFT

ppa. Fenske i.V. Lapice

ppa. Fenske i.V. Lapice

To the Commissioner of Patents

AU9171072

(12) PATENT ABRIDGMENT (11) Document No. AU-B-71072/91
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 637459

(54) Title
HIGHLY CONCENTRATED EMULSIFIABLE CONCENTRATES OF NEOPHANES AND AZANEOPHANES FOR USE IN PLANT PROTECTION

International Patent Classification(s)
(51)[5] **A01N 025/04** **A01N 031/14** **A01N 043/40** **A01N 043/54** **A01N 055/00**

(21) Application No. : **71072/91** (22) Application Date : **15.02.91**

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(71) Applicant(s)
HOECHST AKTIENGESELLSCHAFT

(72) Inventor(s)
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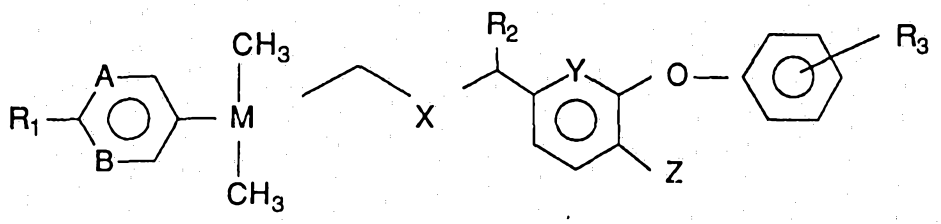
(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(56) Prior Art Documents
AU 71071/92 A01N 25/04
AU 620953 46934/89 A01N 25/04

(57) Claim

1. A highly concentrated emulsifiable concentrate of a compound of the formula I



(I),

in which

A and B = independently of one another are CH,CR_4 and N,

X = CH_2, O, or S,

Y = CH or N,

Z = H or F,

R_1 and R_4 = independently of one another are H, halogen, (C_1-C_3)-alkyl, (C_1-C_3)-halogenoalkyl, (C_1-C_3)-alkoxy, (C_1-C_3)-halogenoalkoxy, (C_1-C_4)-alkylthio, or (C_1-C_4)-halogenoalkylthio, or R_1 and R_4 together are -CH_2-O-CH_2-;

R_2 = H, (C_1-C_3)-alkyl, ethynyl, vinyl, halogen, cyano,

R_3 = H, halogen, (C_1-C_4)-alkyl, (C_1-C_3)-alkoxy and

.../2

M is C or Si, which contain, a combination of 2-4% by weight of an anionic and 4-10% by weight of a nonionic emulsifier with 2-20% by weight of a (C_2-C_{16})-alkanol, said compound of the formula I being present in an amount of 60-90% by weight.

7. A method of combating harmful insects or acarids, which comprises applying an active amount of an emulsifiable concentrate as claimed in one or more of claims 1 to 6 to these or to the plants, areas or substrates infested with these.

637459

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

Name of Applicant : HOECHST AKTIENGESELLSCHAFT

Address of Applicant : D-6230 Frankfurt am Main 80, Federal Republic of Germany

Actual Inventor : HANS ROCHLING

Address for Service : **WATERMARK PATENT & TRADEMARK ATTORNEYS.**
LOCKED BAG NO. 5, HAWTHORN, VICTORIA 3122, AUSTRALIA

Complete Specification for the invention entitled:

HIGHLY CONCENTRATED EMULSIFIABLE CONCENTRATES OF NEOPHANES AND AZANEOPHANES FOR USE IN PLANT PROTECTION

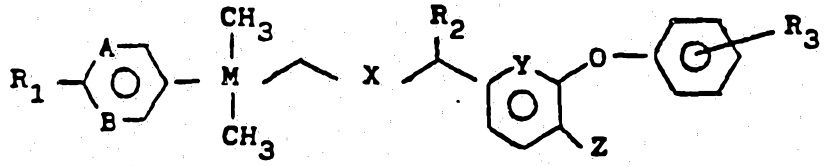
The following statement is a full description of this invention, including the best method of performing it known to :- US

HOECHST AKTIENGESELLSCHAFT HOE 90/F 053 Dr. WS/sch

Description

Highly concentrated emulsifiable concentrates of neophanes and azaneophanes for use in plant protection

The present invention relates to highly concentrated emulsifiable concentrates of compounds of the formula I



(I),

in which

A, B = independently of one another CH, CR_4 or N,
X = CH_2, O or S,
Y = CH or N,
Z = H or F,
R_1 and R_4 = independently of one another H, halogen, (C_1-C_3)-alkyl, (C_1-C_3)-halogenoalkyl, (C_1-C_3)-alkoxy, (C_1-C_3)-halogenoalkoxy, (C_1-C_4)-alkylthio or (C_1-C_4)-halogenoalkylthio, or R_1 and R_4 together = $-CH_2-O-CH_2-$;
R_2 = H, (C_1-C_3)-alkyl, ethynyl, vinyl, halogen or cyano,
R_3 = H, halogen, (C_1-C_4)-alkyl or (C_1-C_3)-alkoxy and
M = C or Si, which contain a combination of an anionic and a nonionic emulsifier with a (C_2-C_{16})-alkanol.

Alkyl and also alkanol contain either a straight-chain or a branched alkyl radical.

Preferably, A and B = CH or N, X = CH_2, R_1 = (C_1-C_3)-alkoxy, R_2 = H, R_3 = H or F and M = Si.

Of the compounds of the formula I, that in which M = Si, R_1 = ethoxy, A and B = CH, X = CH_2, R_2 = H, Y = CH, Z = F and R_3 = H is particularly preferred (Ia).

Active compounds from the group comprising neophanes and azaneophanes (I) have a good plant tolerance and favorable toxicity toward warm-blooded animals, and are suitable for combating animal pests, in particular insects, arachnids and nematodes, which occur in agriculture, in forests, in the preservation of stored products and materials and in the hygiene sector. They are active against normally sensitive and resistant species as against all or individual stages of development (European Patent A-0,224,024, European Patent A-0,249,015 and European Patent A-0,288,810). The conventional types of formulation for insecticides and acaricides are also described in these documents.

Neophanes and azaneophanes can be formulated without major difficulties with a combination of anionic and nonionic emulsifiers using the customary solvents, such as, for example, alkylated benzenes or alkyl naphthalenes to give 10 to 70% strength emulsifiable concentrates which have a good spontaneous emulsifiability in water. However, in the case of higher percent strength, in particular 70 to 85% strength, formulations of the neophanes and azaneophanes (I), which are in the form of viscous oils, it has not been possible to discover concentrates having an adequately spontaneous emulsifiability in water, even using the most diverse solvents and emulsifier combinations.

Thus, using a mixture of Ca phenylsulfonate with ®Emulsogen EL 360 and ®Sapogenat T 200 or of Ca phenylsulfonate with Hoe S 3510 and ®Solvesso 200 (Exxon Chemicals) as the solvent, spontaneously emulsifying concentrates of the neophanes and azaneophanes I can only be prepared if the active compound concentrations are kept within up to 40%.

These same emulsifier/solvent combinations did now show an adequate spontaneous emulsifiability in water when used in higher percent strength, in particular 75 to 85% strength, emulsifiable concentrates. Although a good

emulsion stability was to be achieved after intensive mixing (vigorous shaking or prolonged intensive stirring), preparations which are emulsified in water rapidly and without considerable mechanical effort are required in practice and also by international test specifications (CIPAC, WHO and the like).

An increase in the amount of emulsifier mixture or the use of other proven emulsifier combinations or other solvents brought no improvement (Tab. I).

Table I (Data in % by weight)

Content of compound Ia %	Ca phenylsulfonate % 1)	Emulsogen EL % 2)	Sapogenat T 200 % 3)	Hoe S 3510 % 4)	Emulsogen EL 2.5 % 5)	Solvent %	Spontaneous emulsifiability
19.6	4.3	7.5	2.9			65.7 Solvesso 200	1
19.8	4.2			3.7		72.3 Solvesso 200	1-2
39.0	5.6			6.0		49.4 Solvesso 200	1-2
80.0	3.0			7.0		10.0 Solvesso 200	4
80.0	3.3			7.6		9.1 Solvesso 200	4
80.0	3.9	2.0		7.0		7.1 Solvesso 200	4-5
80.0	3.8			8.6		7.6 Solvesso 200	4
85.0	3.0			7.0		5.0 Solvesso 200	4-5
80.0	3.0			7.0		10.0 N-methylpyrrolidone	4

Content of compound Ia %	Ca phenylsulfonate % 1)	Emulsogen EL % 2)	Sapogenat T 200 % 3)	Hoe S 3510 % 4)	Emulsogen EL 9.5 % 5)	Solvent %	Spontaneous emulsifiability
80.0	3.3			7.7		9.0 N-methylpyrrolidone	4
82.0	3.6			8.4		6.0 N-methylpyrrolidone	4-5
75.0	3.6			8.4		13.0 N-methylpyrrolidone	4
80.0	3.9			7.0	2.0	7.1 N-methylpyrrolidone	4
85.0	3.9			7.0	2.0	2.1 N-methylpyrrolidone	4-5
85.0	3.8			8.7		2.5 N-methylpyrrolidone	4
80.0	3.8			8.7		7.5 N-methyl pyrrolidone	4
80.0	3.0			7.0		10.0 Triacetin	4-5
80.0	3.8			8.7		7.5 Triacetin	4
85.0	3.8			8.7		2.5 Triacetin	4-5

1) Ca phenylsulfonate, Hoechst AG, calcium salt of an alkylarylsulfonic acid (dodecylbenzenesulfonic acid)

2) ®Emulsogen EL, Hoechst AG, fatty acid polyglycol ester, nonionic (36 mol of ethylene oxide (EO)).

3) ®Sapogenat T 200, Hoechst AG, tributylphenol polyglycol ether containing 20 mol of EO.

4) Hoe S 3510, Hoechst AG, block oxyalkylate, nonionic.

5) ®Emulsogen EL 9.5, Hoechst AG.

The rating figures 1-5 have the following meaning:

1 - very good spontaneous emulsifiability
2 - good spontaneous emulsifiability
3 - adequate spontaneous emulsifiability
4 - moderate to poor spontaneous emulsifiability
5 - inadequate spontaneous emulsifiability

Such highly concentrated emulsifiable concentrates would have various ecological and also economic advantages over the customary emulsifiable concentrates having an active compound content of about 10-50%:

- high flash point
- low solvent content and therefore favorable toxicological properties for the user and the environment and
- high profitability, since the despatch and packaging costs are lower for the same amount of active compound.

It has now been found, surprisingly, that if a combination of anionic and nonionic emulsifiers with alcohols as the solvent is used, highly concentrated emulsifiable concentrates of the compounds I, in particular of the compound Ia, which, in addition to having a very good spontaneous emulsifiability, also have a very high emulsion stability, can be obtained.

The formulations according to the invention contain the active compounds of the general formula I to the extent of 60-90% by weight, in particular 70 up to and including 85% by weight.

Anionic emulsifiers which can be used are: salts of dodecylbenzenesulfonic acid, salts of optionally chlorinated (C_{13}-C_{18})-alkanesulfonic acids and furthermore emulsifiers from the group comprising salts of (C_{10}-C_{16})-alkyl-mono- to -hexaglycol ether-sulfates and salts of α-(C_{14}-C_{19})-alkenol-sulfates. It is particularly favorable to use the salts of dodecylbenzenesulfonic acid. The term salts means alkali metal, alkaline earth metal or ammonium salts, in particular Na or Ca salts. The

formulations according to the invention contain the anionic emulsifiers to the extent of 2-4% by weight, preferably 2.5-3.5% by weight.

Nonionic emulsifiers which can be used are: castor oil oxyethylates containing 9 to 40 mol of ethylene oxide (EO); (C_{16}-C_{20})-alkanols which have been reacted with 1 to 15 mol of propylene oxide and then with 1 to 30 mol of ethylene oxide; polymerization products of propylene oxide and ethylene oxide containing 10 to 80% by weight of ethylene oxide and 20 to 90% by weight of propylene oxide; n-butanol-propylene oxide-ethylene oxide block oxyalkylate; xylenol oxyethylate containing 3 to 5 mol of ethylene oxide; ethoxylated (C_8-C_{12})-alkylphenols or propoxylated and ethoxylated tributylphenols. The ethoxylated alkylphenols mentioned preferably contain 8 to 12 mol of ethylene oxide. Propoxylated and ethoxylated tributylphenols are to be understood, in particular, as meaning those which are obtained by reaction of tributylphenols with 8 to 12 mol of propylene oxide and then 1 to 30 mol of ethylene oxide. The n-butanol-propylene oxide-ethylene oxide block oxyalkylate can consist to the extent of 1-3% by weight of n-butanol, to the extent of 40-50% by weight of propylene oxide and to the extent of 50-60% by weight of ethylene oxide. It preferably consists of 2% by weight of n-butanol, 44% by weight of propylene oxide and to the extent of 54% by weight of ethylene oxide (Hoe S 3510, Hoechst AG).

The formulations according to the invention contain these nonionic emulsifiers to the extent of 4-10% by weight, in particular 6-8% by weight.

Mixtures of various anionic and nonionic emulsifiers can also be used according to the invention.

Particularly preferred combination partners for the salts of dodecylbenzenesulfonic acid are the n-butanol-propylene oxide-ethylene oxide block oxyalkylates (for

example Hoe S 3510).

The alcohols (solvents) which can be used according to the invention are either short-chain (C_2-C_3)-alkanols or long-chain (C_4-C_{16})-alkanols. (C_4-C_{12})-alkanols, in particular n-hexanol, are preferably employed because of their higher boiling point and flash point. Mixtures of various alcohols also fulfil the purpose according to the invention. The finished formulations contain the alcohols to the extent of 2-20% by weight, in particular 4-15% by weight.

The combination of a calcium salt of dodecylbenzenesulfonic acid with an n-butanol-propylene oxide-ethylene oxide block oxyalkylate and n-hexanol is particularly preferred for the preparation of highly concentrated emulsifiable concentrates of compounds of the formula I (Ia).

The formulation auxiliaries mentioned are substances which are adequately known to the expert and which are described in the literature (cf. Winnacker-Küchler, "Chemische Technologie (Chemical Technology)", Volume 7, C. Hauser Verlag Munich, 4th Edition, 1986; McCutcheon's, "Detergents and Emulsifiers Annual", MC Publ. Corp., Ridgewood N.J.; Sisley and Wood, "Encyclopedia of Surface Active Agents", Chem. Publ. Co. Inc., N.Y. 1964; and Schönfeldt, "Grenzflächenaktive Äthylenoxidaddukte (Surface-active ethylene oxide adducts)", Wiss. Verlagsgesell., Stuttgart 1976).

Examples of formulations according to the invention are summarized in the following Table II:

Table II (Data in % by weight)

Content of compound Ia %	Ca phenylsulfonate % 1)	Hoe S 3510 % 4)	Emulsogen EL 9.5 % 5)	Solvent %	Spontaneous emulsifiability
80.0	3.0	7.0		10.0 n-butanol	3
85.0	3.0	7.0		5.0 n-butanol	3-4
80.0	3.0	7.0		10.0 isobutanol	3
85.0	3.0	7.0		5.0 isobutanol	3
80.0	2.9	7.1		10.0 2-ethylhexanol	2-3
80.0	3.0	7.0		10.0 n-pentanol	2-3
80.0	3.0	7.0		10.0 n-hexanol	2
85.0	3.0	7.0		5.0 n-hexanol	2
80.0	3.3	7.0		7.7 n-hexanol	2-3
80.0	3.3	7.7		9.0 n-hexanol	2
80.0	2.8	6.6		10.6 n-hexanol	1-2
85.0	2.9	6.7		5.4 n-hexanol	1-2
82.0	2.9	6.7		8.4 n-hexanol	1
78.0	2.8	6.6		12.6 n-hexanol	1

The emulsifiable concentrates listed in Tables I and II were prepared by the customary method, i.e. by simple mixing of the starting components in a stirred flask (cf. Winnacker-Küchler, "Chemische Technologie (Chemical Technology)".

The invention is explained by the following preparation examples:

The individual components are mixed in a stirred flask.

I. 85.00 % by weight of a compound of the formula I
3.00 % by weight of Ca phenylsulfonate[1)]
7.00 % by weight of Hoe S 3510[4)]
5.00 % by weight of isobutanol

The mixture is homogenized by stirring for about 1 hour. A clear solution is then obtained, which shows an adequate spontaneous emulsifiability in a 2% strength dilution in CIPAC standard water D (CIPAC Handbook Volume I (1970), page 878) of 30°C. (Rating figure 3)

II. 80.00 % by weight of a compound of the formula I
2.90 % by weight of Ca phenylsulfonate[1)]
7.10 % by weight of Hoe S 3510[4)]
10.00 % by weight of 2-ethylhexanol

are homogenized as described under I until a clear solution is obtained.
A good to adequate spontaneous emulsifiability is observed on preparation of a 5% strength spray liquor in CIPAC standard water D of 30°C. (Rating figure 2-3)

III. 82.00 % by weight of a compound of the formula I
2.90 % by weight of Ca phenylsulfonate[1)]
6.70 % by weight of Hoe S 3510[4)]
8.40 % by weight of n-hexanol

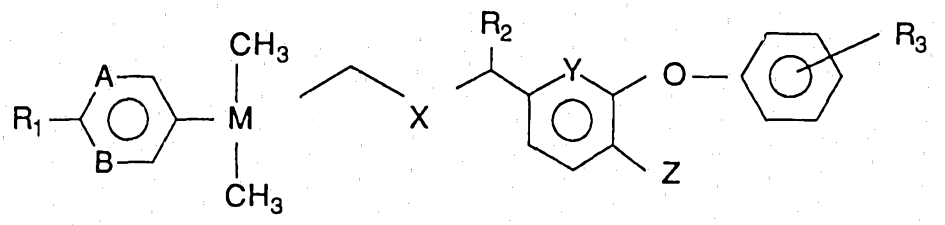
are homogenized as described under I until a clear

solution is obtained.

When used at 2 to 5% strength in CIPAC standard water D of 30°C, a very good spontaneous emulsifiability is found. (Rating figure 1)

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A highly concentrated emulsifiable concentrate of a compound of the formula I



(I),

in which

A and B = independently of one another are CH,CR_4 and N,

X = CH_2, O, or S,

Y = CH or N,

Z = H or F,

R_1 and R_4 = independently of one another are H, halogen, (C_1-C_3)-alkyl, (C_1-C_3)-halogenoalkyl, (C_1-C_3)-alkoxy, (C_1-C_3)-halogenoalkoxy, (C_1-C_4)-alkylthio, or (C_1-C_4)-halogenoalkylthio, or R_1 and R_4 together are -CH_2-O-CH_2-;

R_2 = H, (C_1-C_3)-alkyl, ethynyl, vinyl, halogen, cyano,

R_3 = H, halogen, (C_1-C_4)-alkyl, (C_1-C_3)-alkoxy and

M is C or Si, which contain, a combination of 2-4% by weight of an anionic and 4-10% by weight of a nonionic emulsifier with 2-20% by weight of a (C_2-C_{16})-alkanol, said compound of the formula I being present in an amount of 60-90% by weight.

2. An emulsifiable concentrate as claimed in claim 1, in which, in formula I, A and B = CH or N, X = CH_2, R_1 = (C_1-C_3)-alkoxy, R_2 is H, R_3 is H or F and M = Si.

3. An emulsifiable concentrate as claimed in claim 1 or 2, in which in formula I, M = Si, R_1 = ethoxy, A and B = CH, X = CH_2, R_2 = H, Y = CH, Z = F and R_3 = H.

4. An emulsifiable concentrate as claimed in one or more of claims 1 to 3, which contains 70-85% by weight of a compound of the formula I, 2.5%-3.5% by

weight of an anionic emulsifier, 6-8% by weight of a nonionic emulsifier and 4-15% by weight of an alcohol.

5. An emulsifiable concentrate as claimed in one or more of claims 1 to 4, in which an alkali metal or alkaline earth metal salt of dodecylbenzenesulfonic acid is used as the anionic emulsifier, and n-butanol-propylene oxide-ethylene oxide block oxyalkylate is used as the nonionic emulsifier and a (C_4-C_{12})-alkanol is used as the solvent.

6. An emulsifiable concentrate as claimed in one or more of claims 1 to 5, in which n-hexanol is used as the solvent.

7. A method of combating harmful insects or acarids, which comprises applying an active amount of an emulsifiable concentrate as claimed in one or more of claims 1 to 6 to these or to the plants, areas or substrates infested with these.

8. The use of an emulsifiable concentrate as claimed in one or more of claims 1 to 6 for combating harmful insects or acarids.

DATED this 16th day of February 1993.

HOECHST AKTIENGESELLSCHAFT

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DBM/KJS/BAS AU7107291.WPC DOC 30