Title: USE OF PHOSPHATED ALKANOLS AS DISPERSANTS, EMULSIFIERS, HYDROTROPES, WETTING AGENTS AND COMPATABILITY AGENTS IN AGRICULTURAL COMPOSITIONS

Abstract: The present invention relates to the use of phosphated 2-propylheptanol, phosphated 2-propylheptanol alkoxylate and/or mixtures thereof in agricultural formulations. The invention also relates to agricultural formulations comprising the aforementioned adjuvants, and to methods of treating a plant with the agricultural formulations of the invention.
USE OF PHOSPHATED ALCOHOLS AS DISPERSANTS, EMULSIFIERS, HYDROTROPES, WETTING AGENTS AND COMPATIBILITY AGENTS IN AGRICULTURAL COMPOSITIONS

The present invention relates to the use of phosphated 2-propylheptanol or a phosphated 2-propylheptanol alkoxylate as an adjuvant in agricultural formulations. More specifically, it relates to the use of phosphated hydroxyl compounds as a dispersant, emulsifier, hydrotrope, wetting agent, compatibility agent and the like in agricultural formulations.

Background of the Invention

The agricultural chemical formulator has the difficult task of creating a product that balances bioefficacy, toxicity, cost, shelf life and user friendliness. Of particular importance to the activity of an agricultural formulation is the ability of an aqueous solution to spread evenly over a surface, the so-called wetting ability, and the effective uptake of the active ingredient by the plant to be treated. For example, in agricultural formulations, efficacy benefits from a good wetting of the plant surface and uptake of the active ingredient.

Adjuvants are added to agricultural formulations to improve activity, thereby reducing the amounts of active ingredients necessary, resulting in lower application cost. They generally take the form of surface-active or salt-like compounds and depending on their mode of action, they are classified as modifiers, activators, fertilizers and/or pH buffers.

Surfactants are generally regarded as modifiers and/or activators as they improve wetting properties and uptake of the active ingredients in the agricultural formulation. Additionally, some surfactants improve the solubility of active ingredients in formulations thereby eliminating serious issues such as product separation and/or crystallization.

Anionic, cationic, amphoteric and nonionic surfactants are all known and used in agricultural applications depending on the desired effect. For
example, nonionic surfactants are known to be good wetting agents, and are
often present in agricultural formulations. Many nonionic surfactants are not
soluble enough in solutions with a high amount of electrolytes, such as alkali
and/or alkaline complexing agents, salts, and the like and therefore need the
presence of a hydrotrope to improve the solubility. A number of hydrotropes for
nonionic surfactants have been described in various publications. Examples of
such hydrotropes are ethanol, sodium xylene sulphonate, sodium cumene
sulphonate, alkyl glycosides, and phosphated alkoxylated alcohols.

However, there is still a need for new efficient surfactants that can
improve activity, act as effective hydrotropes, and are compatible for the
achievement of stable formulations delivering optimal performance. The
objective of the present invention is, therefore, to find a new hydrotrope that is
efficient in formulating agricultural compositions, which compositions will remain
homogeneous upon dilution, and where the performance of the compositions is
good.

Accordingly, it is an object of the present invention to provide an
improved agricultural adjuvant. It is also an object of the invention to provide a
stable, agricultural formulation having improved activity. These and other
objects are achieved by the adjuvants/formulations of the present invention.

**Summary of the Invention**

The present invention relates to the use of phosphated 2-
propylheptanol, phosphated 2-propylheptanol alkoxylate and/or mixtures thereof
as agricultural adjuvants. The invention also relates to agricultural formulations
comprising same, and to methods of treating a plant with the agricultural
formulations of the invention.

**Detailed Description of the Invention**

The invention relates to the use of phosphated 2-propylheptanol or
phosphated 2-propylheptanol alkoxylates as a hydrotrope in agricultural
formulations. More specifically, it relates to an agricultural adjuvant that comprises at least one phosphated hydroxyl compound. The adjuvant of the invention can effectively be utilized as a dispersant, emulsifier, hydrotrope, wetting agent, compatibility agent and/or the like in agricultural formulations.

In this regard, the inventors have found that phosphated 2-propylheptanol or a phosphated 2-propylheptanol alkoxylate where the alkoxylate on the average comprises 1-20, preferably 1-15, more preferably 2-10, and most preferably 2-6 ethyleneoxy units and 0-3, preferably 0-2 propyleneoxy and/or butyleneoxy units, is an efficient hydrotrope and activity improver in agricultural formulations.

The adjuvants of the invention improve wetting and uptake of active ingredients by a plant, resulting in a higher activity at a given application rate.

In another embodiment, the invention relates to aqueous agricultural formulations comprising at least one agricultural active, and 0.1-30, preferably 0.1-20, and most preferably 0.1-10% by weight of the adjuvant of the present invention.

The adjuvants of the invention can be used with any active ingredient in order to improve efficacy by improving the dispersion or emulsions properties in the application tank, or modifying the spreading and/or penetration properties of the spray solution on the plant. Examples of active ingredients include, but are not limited to herbicides, fungicides, insecticides, plant growth regulators and the like.

The following is a non-limiting list of active ingredients that can be employed:

- **amide herbicides**
  - allidochlor
  - beflubutamide
  - benzadox
  - benzipram
  - bromobutide
  - cafensfrole
  - CDEA
  - cyprazole
dimethenamid
  dimethenamid-P
diphenamid
epronaz
etnipromid
fentrazamide
fluopoxam
fomesafen
halosafen
isocarbamid
isoxaben
napropamide
naphtalam
pethoxamid
propyzamide
quinonamid
tebutam
  o anilide herbicides
    chloranocryl
cisanilide
cloomeprop
cypromid
diflufenican
etobenzanid
fenasulam
flufenacet
flufenican
mefenacet
mefluidide
metamifop
monalide
naproanilide
pentanochlor
picolinafen
propanil
  • arylalanine herbicides
    benzoylprop
    flamprop
    flamprop-M
  • chloroacetanilide herbicides
    acetochlor
    alachlor
    butachlor
    butenachlor
delachlor
diethatyl
dimethachlor
metazachlor
metolachlor
S-metolachlor
pretichlor
propachlor
propiochlor
prynachlor
terbuchlor
thenylchlor
xylachlor

• sulfonanilide herbicides
  benzofluor
  cloransulam
diclosulam
fiorasulam
flumetsulam
metosulam
perfluidone
pyrimisulfan
profuazol

• sulfonamide herbicides
  asulam
carbasulam
fenasulam
oryzalin
penoxsulam

  o thioamide herbicides
    bencarbazone
    chlorthiamid

• antibiotic herbicides
  bilanafos

• aromatic acid herbicides
  o benzoic acid herbicides
    chloramben
dicamba
2,3,6-TBA
tricamba
- pyrimidinyloxybenzoic acid herbicides
  - bispyribac
  - pyriminobac

- pyrimidinylthiobenzoic acid herbicides
  - pyrithiobac

- phthalic acid herbicides
  - chlorthal

- picolinic acid herbicides
  - aminopyralid
  - clopyralid
  - picloram

- quinolinecarboxylic acid herbicides
  - quinclorac
  - quinmerac

- arsenical herbicides
  - cacodylic acid
  - CMA
  - DSMA
  - hexaflurinate
  - MAA
  - MAMA
  - MSMA
  - potassium arsenite
  - sodium arsenite

- benzoylecyclohexanedione herbicides
  - mesotrione
  - sulcotrione

- benzfuranyl alkylsulfonate herbicides
  - benfuresate
  - ethofumesate

- carbamate herbicides
  - asulam
  - carboxazole
  - chlorprocarb
  - dichlormate
  - fenasulam
  - karbutilate
  - terbucarb

- carbanilate herbicides
  - barban
  - BCPC
carbasulam
carbetamide
CEPC
chlorbufam
chlorpropham
CPPC
desmedipham
phenisopham
phenmedipham
phenmedipham-ethyl
propham
sweep

- cyclohexene oxime herbicides
  alloxydim
  butoxydim
  clethodim
cloproxydim
cycloxydim
prooxydim
sethoxydim
tepraloxydim
tralkoxydim

- cyclopropylisoxazole herbicides
  isoxachlorlote
  isoxaflutole

- dicarboximide herbicides
  benzfluazifzone
  cinidin-ethyl
  flumezin
flumiclorac
tflumioxazin
flumipropyn

- dinitroaniline herbicides
  benfluralin
butralin
dintramine
ethalfluralin
fluchloralin
isopropalin
methalpropalin
nitrilin
oryzalin
pendimethalin
prodiolate
- profuralin
trifuralin

- dinitrophenol herbicides
dinofenate
dinoprop
dinosam
dinoseb
dinoterb
DNOC
etinofen
medinoterb

- diphenyl ether herbicides
ethoxyfen
  - nitrophenyl ether herbicides
    - acifluorfen
    - aclonifen
    - bifenox
    - chlormethoxyfen
    - chlornitrofen
    - etnipromid
    - fluorodifen
    - fluoroglycofen
    - floronefrofen
    - fomesafen
    - furylxyfen
    - halosafen
    - lactofen
    - nitrofen
    - nitrofluorfen
    - oxyfluorfen

- dithiocarbamate herbicides
dazomet
metam

- halogenated aliphatic herbicides
  - alorac
  - chloropon
dalapon
fluroprenate
hexachloroacetone
  - iodomethane
  - methyl bromide
monochloroacetic acid
SMA
TCA
• imidazolinone herbicides
  imazamethabenz
  imazamox
  imazapic
  imazapyr
  imazaquin
  imazethapyr

• inorganic herbicides
  ammonium sulfamate
  borax
  calcium chlorate
  copper sulfate
  ferrous sulfate
  potassium azide
  potassium cyanate
  sodium azide
  sodium chlorate
  sulfuric acid

• nitrile herbicides
  bromobonil
  bromoxynil
  chloroxynil
  dichlobenil
  iodobonil
  ioxynil
  pyraclonil

• organophosphorus herbicides
  amiprophos-methyl
  anilofos
  bensulide
  bilanafos
  butamifos
  2,4-DEP
  DMPA
  EBEP
  fosamine
  glufosinate
  glyphosate
  piperophos

• phenoxy herbicides
  bromofenoxim
  clomeprop
  2,4-DEB
  2,4-DEP
difopenten
disul
erbon
tinpromid
fenteracol
trifopsime

  o phenoxycetic herbicides
    4-CPA
    2,4-D

  10
    3,4-DA
    MCPA
    MCPA-thioethyl
    2,4,5-T

  o phenoxybutyric herbicides
    4-CPB
    2,4-DB
    3,4-DB
    MCPB
    2,4,5-TB

  15
  o phenoxypropionic herbicides
    clopropro
    4-CPP
    dichlorprop
      dichlorprop-P

    25
    3,4-DP
    fenoprop
    mecoprop
      mecoprop-P

  • aryloxyphenoxypionic herbicides
    chlorazifop
clodinafop
clofop
cyhalofop
diclofop

    fenoxaprop
      fenoxaprop-P
    fenthiaprop
    fluazifop
      fluazifop-P

    35
    haloxyfop
      haloxyfop-P
    isoxapryrifop
    metamifop
    propaquizafop

    40
- phenylpyrazolylphenyl herbicides
  - fluazolate
  - pyraflufen
- pyridazine herbicides
  - credazine
  - pyridafol
  - pyridate
- pyridazinone herbicides
  - brompyrazone
  - chloridazon
  - dimidazon
  - flufenpyr
  - metflurazon
  - norflurazon
  - oxapyrazon
  - pydanon
- pyridine herbicides
  - aminopyralid
  - clodinafop
  - clompyralid
  - dithiopyr
  - fluoxycypyr
  - haloxydine
  - picloram
  - picolinatene
  - pyridate
  - thiazopyr
  - triclopyr
• pyrimidinediamine herbicides
  ipyramidam
  tioclorim

• quaternary ammonium herbicides
  cyperquat
  diethamquat
  difenzoquat
  diguad
  morfamquat
  paraquat

• thiocarbamate herbicides
  butylate
cycloate
di-allate
  EPTC
esprocarb
  ethiolate
  isopolinate
  methioarbencarb
  molinate
  orbencarb
  pebulate
  prosulfocarb
  pyributicarb
  sulfallate
  thlobencarb
  tiocarbazil
  tri-allate
  vernolate

• thiocarbonate herbicides
  dimexano
  EXD
  proxan

• thiourea herbicides
  methiuron

• triazine herbicides
  dipropetryn
  triaziflam
  trihydroxytriazine

  o chlorotriazine herbicides
    atrazine
    chlorazine
    cyanazine
cyprazine
equinazine
ipazine
mesoprazine
procyazine
proglinazine
propazine
sebuthylazine
simazine
terbuthylazine
trietazine

- methoxytriazine herbicides
  atraton
  methometon
  prometon
  secbumeton
  simeton
  terbumeton

- methylthiotriazine herbicides
  ametryn
  aziprotryne
  cyanatryn
  desmetryn
  dimethametryn
  methoprotryne
  prometryn
  simetryn
  terbutryn

- triazinone herbicides
  ametridione
  amibuzin
  hexazinone
  isomethoizin
  metamitron
  metribuzin

- triazole herbicides
  amitrole
  cafenstrole
  epronaz
  fluoxam

- triazolone herbicides
  amicarbazone
  bencarbazone
  carfentrazone
flucarbazone
propoxycarbazone
sulfentrazone

- triazolopyrimidine herbicides
  cloransulam
dicosulam
florasulam
flumetsulam
metosulam
penoxsulam

- uracil herbicides
  butafenacil
bromacil
flupropacil
isocil
lenacil
terbacil

- urea herbicides
  benzthiazuron
cumyluron
cycluron
dichloralurea
diflufenopyr
isonoruron
isouron
methabenzthiazuron
monisouron
noruron
  - phenylurea herbicides
    anisuron
buturon
chlorbromuron
chloreturon
chlorotoluron
chloroxuron
daimuron
difenoxuron
dimefuron
dluron
fenuron
fluometuron
fluothiuron
isoproturon
linuron
methiuron
methyldymron
metobenzuron
metobromuron
metoxuron
monolinuron
monuron
neburon
parafluron
phenobenzuron
siduron
tetrafluron
thidiazuron

**sulfonylurea herbicides**

- **pyrimidinylsulfonylurea herbicides**
  - amidosulfuron
  - azimsulfuron
  - bensulfuron
  - chlorimuron
cyclosulfamuron
etoxysulfuron
flazasulfuron
flucetosulfuron
flupyrtsulfuron
foramsulfuron
halosulfuron
imazosulfuron
mesosulfuron
nicosulfuron
orthosulfamuron
oxasulfuron
primisulfuron
pyrazosulfuron
rimsulfuron
sulfometuron
sulfosulfuron
trifloxsulfuron

- **triazinylsulfonylurea herbicides**
  - chlorsulfuron
cinosulfuron
ethametsulfuron
idosulfuron
metsulfuron
prosulfuron
thifensulfuron
triasulfuron
tribenuron
triflusulfuron
tritosulfuron

- thiadiazolylurea herbicides
  - buthiuron
  - ethidimuron
  - tebuthiuron
  - thiazafuron
  - thidiazuron

- unclassified herbicides
  - acrolein
  - allyl alcohol
  - azafenidin
  - benazolin
  - bentazon
  - benzobicyclon
  - buthidazole
  - calcium cyanamide
  - cambendichlor
  - chlorfenac
  - chlorfenprop
  - chlorflurazon
  - chlorflurenol
  - cinmethylin
  - clomazone
  - CPMF
  - cresol
  - ortho-dichlorobenzene
  - dimepiperate
  - endothal
  - fluoromidine
  - fluridone
  - flurochloridone
  - flurtamone
  - fluthiacet
  - indanoan
  - methazole
  - methyl isothiocyanate
  - nipyraclofen
  - OCH
  - oxadiargyl
  - oxadiazon
  - oxaziclomefene
  - pentachlorophenol
  - pentoxazone
phenylmercury acetate
pinoxaden
prosulfalin
pyribenzoxim
pyriflidal
quinoclamine
rhodethanil
sulgtycopin
thidiazimin
tridiphane
trimeton
tripropindan
tritac

Fungicides include, but are not limited to:

- **aliphatic nitrogen fungicides**
  butylamine
cymoxanil
dodicin
dodine
quazatine
iminoctadine

- **amide fungicides**
carpromamid
chloranilformethan
cyflufenamid
dicloctmyet
ethaboxam
fenoxanil
flumetover
furametpyr
mandipropamid
penthiopyrad
prochloraz
quinazamid
slihofoam
tritorine

- **acylamino acid fungicides**
benalaxyl
benalaxyl-M
furalaxyl
metalaxyl
metalaxyl-M
pflurazoate

- **anilide fungicides**
benalaxyl
benalaxyl-M
boscalid
carboxin
fenhexamid
metalaaxy
metalaaxy-M
metsulfocox
ofurace
oxadixyl
oxycarboxin
pyracarbolid
thifluzamide
tiadinil

• benzanilide fungicides
  benodonil
  flutolanil
  mebenil
  mepronil
  salicylanilide
tecloftalam

• furanilide fungicides
  fenfuran
  furalaxy
  furcarbanil
  methfuroxam

• sulfonanilide fungicides
  flusulfamide

• benzamide fungicides
  benzohydroxamic acid
  fluopicolide
tioxymid
trichlamide
zarilamid
zoxamide

• furamid fungicides
  cyclafuramid
  furmecyclox

• phenylsulfamide fungicides
dichlofluand
  tolylfualnd

• sulfonamid fungicides
  amisulbrom
cyazofamid

• valinamid fungicides
  benthialalicarb
  iprovalicarb
• antibiotic fungicides
  aureofungin
  blasticidin-S
  cycloheximide
  griseofulvin
  kasugamycin
  natamycin
  polyoxins
  polyoxorim
  streptomycin
  validamycin
  • stroblurin fungicides
    azoxylostrob
    dimoxystrobin
    fluoxastrobin
    kresoxim-methyl
    metominostrobin
    orysastrob
    picoxystrobin
    pyraclostrobin
    trifloxystrobin
• aromatic fungicides
  biphenyl
  chlorodinitronaphthalene
  chloroneb
  chlorothalonil
  cresol
  diconar
  hexachlorobenzene
  pentachlorophenol
  quintozone
  sodium pentachlorophenoxide
  tecnazene
• benzlmidazole fungicides
  benomyl
  carbendazim
  chlorfenazole
  cyperdazole
  debacarb
  fuberidazole
  mecarbinzid
  rabenzazole
  thiabendazole
• benzlmidazole precursor fungicides
  furophanate
  thiophanate
  thiophanate-methyl
• benzothiazole fungicides
  bentaluron
  chlobenthiazone
  TCMTB
  bridged diphenyl fungicides
  bithionol
  dichlorothen
  diphenylamine
• carbamate fungicides
  bentiavalicarb
  furoxanate
  iprovalicarb
  propamocarb
  thiophanate
  thiophanate-methyl
  • benzimidazolylcarbamate fungicides
    benomyl
    carbendazim
    cypermethazole
  debacarb
  mecarbinid
  • carbanilate fungicides
    diethofencarb
• conazole fungicides
  • conazole fungicides (imidazoles)
    cl Pedro
    clotrimazole
    imazalil
    oxpoconazole
  prochloraz
  triflumizole
  see also imidazole fungicides
  • conazole fungicides (triazoles)
    azaconazole
    bromuconazole
    cyproconazole
diclobutrazol
difenoconazole
diniconazole
diniconazole-M
epoxiconazole
etaconazole
fenbuconazole
fluiticonazole
flutriazole
flutriafol
furconazole
furconazole-cis
hexaconazole
imibenconazole
ipconazole
5 metconazole
myclobutanil
penconazole
propiconazole
prothioconazole
10 quinconazole
mimeconazole
tebuconazole
tetraconazole
tridimefon
15 triadimenol
triticonazole
uniconazole
uniconazole-P
see also triazole fungicides

20 • copper fungicides
   Bordeaux mixture
   Burgundy mixture
   Cheshunt mixture
copper acetate
25 copper carbonate, basic
copper hydroxide
copper naphthenate
copper oleate
copper oxychloride
30 copper sulfate
copper sulfate, basic
copper zinc chromate
cufraneb
cuprobam
35 cuprous oxide
mancopper
oxine copper

• dicarboximide fungicides
   famoxadone
fluoromide
   • dichlorophenyl dicarboximide fungicides
      chlozolinate
dichlozoline
iprodione
40 isovaledione
myclozolin
45
procymidone
t vinclozolin
• phthalimide fungicides
captan
• dinitrophenol fungicides
binapacryl
dinobuton
dinocap
dinocap-4
dinocap-6
dinocton
dinopenton
dinosulfon
dinoterbon
DNOC
• dithiocarbamate fungicides
azithiram
carbamoph
cuframeb
cuprobam
disulfiram
ferbam
metam
nabam
tecoram
thiram
ziram
• cyclic dithiocarbamate fungicides
dazomet
etem
milneb
• polymeric dithiocarbamate fungicides
mancoppper
mancozeb
maneb
metiram
polycarbamate
propineb
zineb
• imidazole fungicides
cyazofamid
fenamidone
fenapanil
glyodin  
iprodione  
isovaldione  
pefurazoate  
triazole  
see also conazole fungicides (imidazoles)

- inorganic fungicides  
potassium azide  
potassium thiocyanate  
sodium azide  
sulfur  
see also copper fungicides  
see also inorganic mercury fungicides

- mercury fungicides  
  - inorganic mercury fungicides  
    mercuric chloride  
    mercuric oxide  
    mercurous chloride  
  - organomercury fungicides  
    (3-ethoxypropyl)mercury bromide  
    ethylmercury acetate  
    ethylmercury bromide  
    ethylmercury chloride  
    ethylmercury 2,3-dihydroxypropyl mercaptide  
    ethylmercury phosphate  
    N-(ethylmercury)-p-toluenesulphonanilide  
    hydrargaphen  
    2-methoxyethylmercury chloride  
    methylmercury benzoate  
    methylmercury dicyandiamide  
    methylmercury pentachlorophenoxide  
    8-phenylmercurioxyquinoline  
    phenylmercuriurea  
    phenylmercury acetate  
    phenylmercury chloride  
    phenylmercury derivative of pyrocatechol  
    phenylmercury nitrate  
    phenylmercury salicylate  
    thiomersal  
    tolylmercury acetate

- morpholine fungicides  
  aldimorph  
  benzamor  
  carbamorph  
  dimethomorph  
  dodemorph  
  fenpropimorph
flumorph
tridemorph

- organophosphorus fungicides
  ampropylfos
ditalimfos
difenphos
fosetyl
hexylthiofos
iprobenfos
phosdiphen
pyrazophos
tolclofos-methyl
triadiphos

- organotin fungicides
decafentin
tentin
tributyltin oxide

- oxathiin fungicides
carboxin
oxycarboxin

- oxazole fungicides
  chlozolinate
dichlozoline
drazoxolon
famoxadone
hymexazol
methoxypyr
myclozolin
oxadixyl
vinclozolin

- polysulfide fungicides
  barium polysulfide
calcium polysulfide
potassium polysulfide
sodium polysulfide

- pyrazole fungicides
  furametpyr
penthiopyrad

- pyridine fungicides
  bosalid
buthiobate
dipyrithione
fluazinam
fluopicolide
pyridinitril
pyrifloux
pyroxychlor
pyroxylurfur

- pyrimidine fungicides
  bupirimate
cyprodinil
diflumetorim
dimethirimol
etirimol
fenarimol
femrzone
mepanipyrim
nuarimol
pyrimethanil
triarimol

- pyrrole fungicides
  fenpiclonil
  fludioxonil
  fluoroimide

- quinoline fungicides
  ethoxyquin
  halacrine
  8-hydroxyquinoline sulfate
  quinacetol
  quinoxyfen

- quinone fungicides
  benquinox
  chloranil
  dichlone
dithianon

- quinoxaline fungicides
  chinomethionat
  chlorquinox
  thioquinox

- thiazole fungicides
  ethaboxam
  etridiazole
  metsulfoxvax
  octhilinone
  thiabendazole
thiadifluor
thifluzamide

- thiocarbamate fungicides
  methasulfocarb
  prothiocarb

- thiophene fungicides
  ethaboxam
  silthiofam
• triazine fungicides
  anilazine
• triazole fungicides
  amisulbrom
  bitertanol
  fluotrimazole
  triazbutil
  see also conazole fungicides (triazoles)
• urea fungicides
  bentaluron
  pencycuron
  quinazamid
• unclassified fungicides
  acibenzolar
  acypetacs
  allyl alcohol
  benzalkonium chloride
  benzamacril
  bethoxazin
  carvone
  chloropicrin
  DBCP
dehydroacetic acid
diclomezine
diethyl pyrocarbonate
fenaminosulf
fenitropan
fenpropidin
formaldehyde
furfural
pentachlorobutadiene
jodomethane
isoprothiolane
methyl bromide
methyl isothiocyanate
metrafenone
nitroethylene
nitrohalo-isopropyl
OCH
2-phenylphenol
phthalide
piperalin
probenazole
proquinazid
pyroquillon
sodium orthophenylphenoxide
spiroxamine
sultropen
thicyofen
tricyclazole
zinc naphthenate

Insecticides include, but are not limited to:

- antibiotic insecticides
  allosamidin
  thuringiensin

  - macrocyclic lactone insecticides
    spinosad
      - avermectin insecticides
        abamectin
doramectin
eramectin
eprinomectin
ivermectin
selamectin

- milbemycin insecticides
  lepimectin
milbemectin
milbemycin oxime
moxidectin

- arsenical insecticides
  calcium arsenate
copper acetoarsenite
copper arsenate
lead arsenate
potassium arsenite
sodium arsenite

- botanical insecticides
  anabasine
azadirachtin
d-limonene
nicotine
pyrethrins
cinerins
cinerin I
cinerin II
jasmolin I
jasmolin II
pyrethrin I
pyrethrin II
guassia
rotenone
ryania
sabadilla

- carbamate insecticides
  bendiocarb
carbaryl
    - benzfuranyl methylcarbamate insecticides
      benfuracarb
carbofuran
carbosulfan
decarbofuran
furathiocarb
    - dimethylcarbamate insecticides
dimetan
dimetilan
hyquincarb
primicarb
    - oxime carbamate insecticides
alany carb
al dicarb
aldoxycarb
butoxycarb oxide
methomyl
nitrilacarb
oxamyl
tazimcarb
thiocarboxime
thiodicarb
thiofanox
    - phenyl methylcarbamate insecticides
allyxycarb
aminocarb
bufencarb
butacarb
carbonolate
clothecarb
dicresyl
dioxacarb
EMPC
ethiofencarb
denetacarb
fenobucarb
isoprocarb
methiocarb
metolcarb
mexacarbate
promacyl
promecarb
propoxur
trimethacarb
XMC
xylotylcarb

- dinitrophenol insecticides
dinex
dinoprop
dinosam
DNOC

- fluorine insecticides
  barium hexafluorosilicate
cryolite
  sodium fluoride
  sodium hexafluorosilicate
  sulfluramid

- formamidine insecticides
  amitraz
  chlordimeform
  formetanate
  formparanate

- fumigant insecticides
  acrylonitrile
  carbon disulfide
  carbon tetrachloride
  chloroform
  chloropicrin
  para-dichlorobenzene
  1,2-dichloropropane
  ethyl formate
  ethylene dibromide
  ethylene dichloride
  ethylene oxide
  hydrogen cyanide
  iodomethane
  methyl bromide
  methylchloroform
  methylene chloride
naphthalene
phosphine
sulfuryl fluoride
tetrachloroethane

- inorganic insecticides
  - borax
  - calcium polysulfide
  - copper oleate
  - mercurous chloride
  - potassium thiocyanate
  - sodium thiocyanate
  - see also arsenical insecticides
  - see also fluorine insecticides

- insect growth regulators
  - chitin synthesis inhibitors
    - bifenthrin
    - buprofezin
    - chlorfluazonuron
    - cyromazine
  - diflubenzuron
  - flucyloxyuron
  - flufenoxuron
  - hexaflumuron
  - lufenuron
  - novaluron
  - noviflumuron
  - penfluron
  - teflubenzuron
  - triflumuron

- juvenile hormone mimics
  - epofenonane
  - fenoxycarb
  - hydroprene
  - kinoprene
  - methoprene
  - pyriproxyfen
  - triprenone

- juvenile hormones
  - juvenile hormone I
  - juvenile hormone II
  - juvenile hormone III

- moulting hormone agonists
  - chromafenozide
halofenozide
methoxyfenozone
tebufenozide

- moulting hormones
  - α-ecdysone
  - ecdysterone

- moulting inhibitors
  - diofenolan

- precocenes
  - precocene I
  - precocene II
  - precocene III

- unclassified insect growth regulators
dicyclanil

- nereistoxin analogue insecticides
  - bensultap
cartap
thiocyclam
thiosultap

- nicotinoid insecticides
  - fionicamid

  - nitroguanidine insecticides
    - clothianidin
dinofuran

  - imidacloprid
thiamethoxam

  - nitromethylene insecticides
    - nitenpyram
nithiazine

  - pyriproxyfenylmethylamine insecticides
    - acetamiprid
imidacloprid
nitenpyram
thiacloprid

- organochlorine insecticides
  - blemo-DDT
camphechlor
DDT
  - pp'-DDT
ethyl-DDD
HCH
  gamma-HCH
  lindane
  methoxychlor
  pentachlorophenol
TDE
  o cyclodiene insecticides
    aldrin
    bromocyclen
    chlorbicyclen
    chlordane
    chlordecone
    dieldrin
    dillor
    endosulfan
    endrin
    HEOD
    heptachlor
    HHDN
20  isobenzan
    isodrin
    kelevan
    mirex
• organophosphorus insecticides
25  o organophosphate insecticides
    bromfenvinfos
    chlorfenvinphos
    crotodyphos
    dichlorvos
    dicrotophos
    dimethyldinphos
    fospirate
    heptenophos
    methocrotophos
30  mevinphos
    monocrotophos
    naled
    naftalofos
    phosphamidon
35  propaphos
    TEPP
    tetrachlorvinphos
  o organothiophosphate insecticides
    dioxabenzofos
fosmethilan
phenothoate

- **aliphatic organothiophosphate insecticides**
  - acethion
  - amiton
  - cadusafos
  - chlorethoxyfos
  - chloromethozone
  - demephion-O
  - demephion-S
  - demeton
  - demeton-O
  - demeton-S
  - demeton-methyl
    - demeton-O-methyl
    - demeton-S-methyl
  - demeton-S-methylsulphon
  - disulfoton
  - ethion
  - ethoprophos
  - IPSP
  - isothioate
  - malathion
  - methacrifos
  - oxydemeton-methyl
  - oxydeprofos
  - oxydisulfoton
  - phorate
  - sulofetep
  - terbufos
  - thiometon

- **aliphatic amide organothiophosphate insecticides**
  - amidithion
  - cyanthoate
  - dimethoate
  - ethoate-methyl
  - formothion
  - mecarbam
  - omethoate
  - prothoate
  - sophamide
  - vanidothion
- oxime organothiophosphate insecticides
  chlorphoxim
  phoxim
  phoxim-methyl

  - heterocyclic organothiophosphate insecticides
    azamethiphos
    coumaphos
    coumichoate
    dioxathion
    endothion
    menazon
    morphothion
    phosalone
    pyraclofos
    pyridaphenthion
    quinothion

  - benzothiopyran organothiophosphate insecticides
    dithicrofos
    thicrofos

  - benzotriazine organothiophosphate insecticides
    azinphos-ethyl
    azinphos-methyl

  - isoindole organothiophosphate insecticides
    dialifos
    phosmet

  - isoxazole organothiophosphate insecticides
    isoxathion
    zolaprofos

  - pyrazolopyrimidine organothiophosphate insecticides
    chlorprazophos
    pyrazophos

  - pyridine organothiophosphate insecticides
    chlorpyrifos
    chlorpyrifos-methyl

  - pyrimidine organothiophosphate insecticides
    butathiofos
    diazinon
    etrimfos
    lirimfos
pirimiphos-ethyl
pirimiphos-methyl
primidophos
pyrimethane
tebupirimfos

- quinoxaline organothiophosphate insecticides
  quinalphos
  quinalphos-methyl

- thiadiazole organothiophosphate insecticides
  athidathion
  lythidathion
  methidathion
  prothidathion

- triazole organothiophosphate insecticides
  isazofos
  triazophos

- phenyl organothiophosphate insecticides
  azothoate
  bromophos
  bromophos-ethyl
  carbophenothion
  chlorothiophos
  cyanophos
  cythioate
  dicapthion
  dichlofenthion
  etaphos
  famphur
  fenchlorphos
  fenitrothion
  fensulfothion
  fenthion
  fenthion-ethyl
  heterophos
  iodphenphos
  mesulfenfos
  parathon
  parathion-methyl
  phenkapton
  phosnicchlor
  profenofos
  prothiofos
  sulprofos
  temephos
trichlorometaphos-3
trifenofos

- phosphonate insecticides
  - butonate
  - trichlorfon

- phosphonothioate insecticides
  - mecarphon
    - phenyl ethylphosphonothioate insecticides
      - fenofos
      - trichloronat
    - phenyl phenylphosphonothioate insecticides
      - cyanofenphos
      - EPN
      - leptophos

- phosphoramide insecticides
  - crufoamate
  - fenamiphos
  - fosthietan
  - methosfolan
  - pirimethan

- phosphoramidothioate insecticides
  - acephate
  - isocarbophos
  - isofenphos
  - methamidophos
  - propetamphos

- phosphorodiamide insecticides
  - dimefox
  - mazidox
  - mipafox
  - schradan

- oxadiazine insecticides
  - indoxacarb

- phthalimide insecticides
  - dialfos
  - phosmet
  - tetramethrin

- pyrazole insecticides
  - acetoprole
ethiprole
fipronil
pyrafluprole
pyriproxyfen
tebufenpyrad
tolifenpyrad
vaniliprole

- pyrethroid insecticides
  - pyrethroid ester insecticides
    - acrinathrin
    - allethrin
      - bioallethrin
    - barthrin
    - bifenthrin
    - bioethanomethrin
cyathrin
cycloprothrin
cyfluthrin
  - beta-cyfluthrin
cyhalothrin
gamma-cyhalothrin
  - lambda-cyhalothrin
cypermethrin
  - alpha-cypermethrin
  - beta-cypermethrin
  - theta-cypermethrin
  - zeta-cypermethrin
cyphenothrin
deltamethrin
dimefluthrin
dimethrin
demethrin
dempenthrin
fenfluthrin
fenpiprin
fenpropathrin
tau-fluvinate
furethrin
imiprost
metofluthrin
permethrin
biopermethrin
transpermethrin
phenothrin
prallethrin
profluthrin
pyresmethrin
resmethrin
bioresmethrin
cismethrin
tefluthrin
terallethrin
tetramethrin
tralomethrin
transfluthrin

- pyrethroid ether insecticides
  etofenprox
  flufenprox
  halfenprox
  protrifenbute
  silafluofen

- pyrimidinamine insecticides
  flufenerim
  pyrimidifen

- pyrrole insecticides
  chlorfenapyr

- tetronic acid insecticides
  spiromesifen
  spirotetramat

- thiourea insecticides
  diafenbenuim

- urea insecticides
  flucofurone
  sulcofurone
  see also chitin synthesis inhibitors

- unclassified insecticides
  closantel
  crotamiton
  EXD
  fenazaflor
  fenoxacrim
  fluendiamide
  hydramethylnon
  isoprothiolane
  malonobenz
metaflumizone
methoxadiazone
nifuridide
pyridaben
pyridalyl
rafoxanide
triarathene
triazamate

Plant growth regulators include, but are not limited to:

- **antiauxins**
  - clofibric acid
  - 2,3,5-tri-iodobenzoic acid

- **auxins**
  - 4-CPA
  - 2,4-D
  - 2,4-DB
  - 2,4-DEP
dichlorprop
fenoprop
IAA
IBA
naphthaleneacetamide
α-naphthaleneacetic acid
1-naphthol
naphthoxyacetic acid
potassium naphthenate
sodium naphthenate
2,4,5-T

- **cytokinins**
  - 2iP
  - benzyladenine
  - kinetin
  - zeatin

- **defoliants**
  - calcium cyanamide
dimethipin
endothall
ethephon
merphos
metoxuron
pentachlorophenol
thidiazuron
tribufos
- ethylene inhibitors
  - aviglycine
  - 1-methylcyclopropene

- ethylene releasers
  - ACC
  - etacelasil
  - ethephon
  - glyoxime

- gibberellins
  - gibberellins
  - gibberellic acid

- growth inhibitors
  - abscisic acid
  - ancymidol
  - butralin
  - carbaryl
  - chlorphonium
  - chlorpropham
  - dikegulac
  - flumetralin
  - fluoridamid
  - fosamine
  - glyphosine
  - isopyrimol
  - jasmonic acid
  - maleic hydrazide
  - mepiquat
  - piproctanyl
  - prohydrojasmon
  - propham
  - 2,3,5-tri-iodobenzoic acid
    - morphactins
      - chlorfluoren
      - chlorfluorenol
    - dichlorfluorenol
    - fluorenol

- growth retardants
  - chlorimequat
  - daminozide
  - flurprimidol
  - mefluidide
  - paclobutrazol
  - tetcyclacis
  - uniconazole
• growth stimulators
  brassinolide
  forchlorfenuron
  hymexazol

• unclassified plant growth regulators
  benzofluor
  buminafos
  carvone
  ciobutide
  clofencet
  cloxyfonac
  cyclanilide
  cycloheximide
  epocholeone
  ethychlozate
  ethylene
  fenridazon
  heptopargil
  holosulf
  inabenfide
  karetazan
  lead arsenate
  methasulfocarb
  prohexadione
  pydanon
  sintofen
  triapenthenol
  trinexapac

The adjuvant of the invention comprises phosphated 2-propylheptanol and/or a phosphated 2-propylheptanol alkoxylation, where the alkoxylation on average comprises 1-20, in another embodiment 2-10, in still another embodiment 2-6, and in still another embodiment 2-4, and most preferably 3, ethyleneoxy units and 0-3, preferably 0-2, propyleneoxy units. In one embodiment, the adjuvant of the invention comprises at least one phosphated alkoxylation according to the formula

\[
\text{OM} \\
C_3H_7 \\
\text{OM} \\
\text{H}_2C\left(\text{CH}_2\right)_2\text{CH}-\text{H}_2\text{O}\left(\text{CH}_2\text{CH}_2\text{O}\right)_5\text{P}-\text{OM} \quad (\text{II})
\]
where M is H, a monovalent metal ion or R₁R₂R₃R₄N⁺, where R₁, R₂, R₃, and R₄ are H, an alkyl group with 1-4 carbon atoms or –CH₂CH₂OH, and c is a number 1-20, preferably 2-10, more preferably 2-6, even more preferably 2-4, and most preferably 3.

Phosphated 2-propylheptanol or a phosphated 2-propylheptanol alkoxylate may be obtained by different processes, the most common being the reaction of 2-propylheptanol or alkoxylated 2-propylheptanol with polyphosphoric acid or phosphorous pentoxide (P₂O₅).

In the process using polyphosphoric acid the resulting product mixture will predominantly contain the monoalkylphosphate ester of 2-propylheptanol or of alkoxylated 2-propylheptanol and only a small amount (<10%) of the dialkylphosphate ester. Always rather large amounts of inorganic phosphate residues from the polyphosphoric acid, such as orthophosphoric acid, will be present.

When P₂O₅ is used as the phosphatising reagent and the molar ratio between P₂O₅ and alcohol or alkoxylated alcohol is 1:3, the product mixture will contain about equal amounts of monoalkylphosphate ester and dialkylphosphate ester, and only smaller amounts of inorganic phosphate residues. A larger amount of alcohol or alkoxylated alcohol will yield more diester, and a smaller amount will yield more monoester. It will be known to a person skilled in the art how to synthesise phosphate esters with certain amounts of mono- and dialkyl phosphate esters. For a general description of phosphate esters see, e.g., *Anionic Surfactants* Vol. 7, Part II, pages 504-511 in *Surfactant Science Series*, edited by Warner M. Linfield, Marcel Dekker Inc., New York and Basle 1976. The alcohol alkoxylates to be phosphated may be either of the standard type produced by using an alkaline catalyst such as KOH, or of the narrow range type produced by using a narrow range catalyst, such as an acid catalyst, Ca(OH)₂ or hydrotalcite.
If necessary, the reaction mixture resulting from either of the procedures can be neutralized by an organic or inorganic base before use. The base may be, e.g., an alkali hydroxide, such as sodium hydroxide or potassium hydroxide; ammonia, an alkanolamine, such as monoethanolamine, triethanolamine or methyloltriethanolamine; or an alkylamine such as triethylamine.

The monoalkylphosphate ester of 2-propylheptanol or of ethoxylated 2-propylheptanol has the formula

\[
\begin{align*}
H_3C-\left(\begin{array}{c}
\text{OM} \\
C_6H_{13}
\end{array}\right)CH-CH_2O\left(\begin{array}{c}
\text{OM} \\
O
\end{array}\right)\text{OM} \\
\text{OM}
\end{align*}
\tag{II}
\]

where M is H, a monovalent metal ion or R_1R_2R_3R_4N^+, where R_1, R_2, R_3, and R_4 are H, an alkyl group with 1-4 carbon atoms or \(-\text{CH}_2\text{CH}_2\text{OH}\), and c is a number 0-20, preferably 2-10, more preferably 2-6, even more preferably 2-4, and most preferably 3. The product mixture resulting from the reaction of 2-propylheptanol or of ethoxylated 2-propylheptanol with polyphosphoric acid may also contain smaller amounts of products containing more than one phosphate unit according to the formula

\[
\begin{align*}
H_3C-\left(\begin{array}{c}
\text{OM} \\
C_9H_{17}
\end{array}\right)CH-CH_2\left(\begin{array}{c}
\text{OM} \\
O
\end{array}\right)\left(\begin{array}{c}
\text{OM} \\
O
\end{array}\right)\left(\begin{array}{c}
\text{OM} \\
O
\end{array}\right)\left(\begin{array}{c}
\text{OM} \\
O
\end{array}\right)\left(\begin{array}{c}
\text{OM} \\
\text{OM}
\end{array}\right) \\
\text{OM}
\end{align*}
\tag{III}
\]

where n is 1-3 and M and c have the same meaning as above.

For ethoxylates containing smaller amounts of ethyleneoxy units, also a certain amount of unethoxylated product will remain due to the distribution of ethyleneoxy units. This unethoxylated product will also be phosphatised during the reaction with the phosphatising agent, and thus the phosphate ester of 2-propylheptanol will also be present in the reaction mixture resulting from these above-mentioned ethoxylates.

The dialkylphosphate ester of 2-propylheptanol has the formula
where M and c have the same meaning as above. The product mixture resulting from the reaction of 2-propylheptanol or ethoxylated 2-propylheptanol with P₂O₅ may also contain a dialkyl diphasphate ester according to the formula

\[
\text{H}_3\text{C}-(\text{CH}_2)_4\text{C}-(\text{CH}_2)_7\text{O}-(\text{CH}_2\text{CH}_2\text{O})_c\text{P}(\text{O}-\text{CH}_2\text{CH}_2\text{O})_c\text{P}(\text{O}-\text{CH}_2\text{CH}_2\text{O})_c\text{C}_7\text{H}_3 \tag{IV}
\]

where M and c have the same meaning as above. This type of diester may be hydrolysed to yield 2 moles of monoester.

2-Propylheptanol is normally made by a process resulting in small amounts of by-products such as 4-methyl-2-propylhexanol and 5-methyl-2-propylhexanol. These products or their ethoxylates will also be phosphated during the process, and the phosphated species will be comprised in the resulting product mixture.

The reaction mixtures obtained by the phosphatising procedures are normally used as such without any purification procedure, but both the mixtures and the purified phosphate esters function as hydrotrones. To act as a good hydrotrone, the mixture should predominantly contain the monoalkyl phosphate esters, since these are better hydrotrones than the dialkyl phosphate esters. Preferably more than 60, more preferably more than 70, and most preferably more than 80% by weight of the mixture should be monoalkyl phosphate esters.

The phosphated 2-propylheptanol or phosphated 2-propylheptanol alkoxylates where the alkoxylate on average comprises 1-20, preferably 2-10, more preferably 2-6, even more preferably 2-4, and most preferably 3, ethyleneoxy units and 0-3, preferably 0-2, propyleneoxy and/or butyleneoxy,
preferably propyleneoxy, units described above and a process for their production are already partly disclosed in the earlier mentioned publications EP-A-256427 and CH-A-481953 for use as dispersants for pigments and as additives in an emulsion polymerisation process, respectively. However, the phosphated 2-propylheptanol alkoxylate where the alkoxylate comprises 2-4, preferably 3, ethyleneoxy units on average is especially efficient as a hydrotrope compared to the other phosphated alkoxylates of 2-propylheptanol (see Table 1 in the Examples). Therefore, the invention also relates to the phosphated 2-propylheptanol alkoxylate where the alkoxylate on average comprises 2-4, preferably 3, ethyleneoxy units *per se* and a process for its production.

The agricultural formulations of the invention may contain alkali, preferably sodium or potassium hydroxide, and an alkaline complexing agent that may be inorganic as well as organic. Typical examples of inorganic complexing agents used in the alkaline composition are alkali salts of silicates and phosphates such as sodium silicate, sodium metasilicate, sodium tripolyphosphate, sodium orthophosphate, sodium pyrophosphate, and the corresponding potassium salts. Typical examples of organic complexing agents are alkaline aminopolyphosphonates, organic phosphates, polycarboxylates, such as citrates; aminocarboxylates, such as sodium nitrilotriacetate (Na₃NTA), sodium ethylenediaminetetraacetate (EDTA), sodium diethylenetriaminepentacacetate, sodium 1,3-propylenediaminetetraacetate, and sodium hydroxyethyl ethylenediaminetriacetate. The amount of alkali present in the composition depends on the application and on whether the composition is a concentrate or a ready-to-use solution.

The concentrated compositions of the present invention are stable and in many cases generally clear. The clarity interval is suitably between 0-40°C, preferably between 0-50°C, and most preferably between 0-60°C. This may be adapted by changing the ratio of hydrotrope to nonionic surfactant. The
concentrate normally contains 50-95% by weight of water, suitably 70-90% by weight.

To obtain a ready-to-use solution the concentrates are diluted with water and/or fertilizer solutions up to 1:40. The diluted solutions are also clear and stable, but in some cases they may turn a little bit hazy although they are still stable and do not separate. The ready-to-use solutions exhibit good properties. A typical concentrate formulation contains 3-5% by weight of the adjuvant according to the present invention, while a ready-to-use formulation would normally contain 0.2-1% by weight of same.

Tank mixes can include multiple pesticides mixed together, targeting multiple pests, while using water as the delivery medium. In that case the adjuvant would help prevent incompatibilities that could occur when mixing different formulation types together, such as emulsifiable concentrates and suspension concentrates.

Tank mixes can also include pesticide(s) dispersed or emulsified in a fertilizer solution. The adjuvants of the present invention function to facilitate the dispersion or emulsification of the pesticide(s) in the salt solutions by coupling the surfactants into the electrolyte solution.

The present invention is further illustrated by the following Examples.

**Example 1**
This example relates to a comparison between phosphated 2-propylheptanol + 5 EO and phosphated hexanol + 5 EO as hydrotropes for 2-propylheptanol + 5 EO.
Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formulation A</th>
<th>Formulation B (Comparison)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphated 2-PH+5EO</td>
<td>3.5%</td>
<td></td>
</tr>
<tr>
<td>Phosphated hexanol+5EO</td>
<td></td>
<td>4.9%</td>
</tr>
<tr>
<td>2-PH+5EO</td>
<td>5.0%</td>
<td>5.0%</td>
</tr>
<tr>
<td>Sodium metasilicate</td>
<td>4.0%</td>
<td>4.0%</td>
</tr>
<tr>
<td>Tetrapotassium pyrophosphate</td>
<td>6.0%</td>
<td>6.0%</td>
</tr>
<tr>
<td>Water</td>
<td>81.5%</td>
<td>80.1%</td>
</tr>
</tbody>
</table>

A smaller amount of phosphated 2-propylheptanol+5EO, as compared to phosphated hexanol+5EO, was required to obtain a clarity interval of 0-60°C. The formulations with phosphated 2-propylheptanol + 5 EO as a hydrotrope were also much more stable upon dilution.

Example 2

This example compares a number of phosphated ethoxylated alcohols with phosphated 2-propylheptanol + 5 EO as a hydrotrope for 2-propylheptanol + 5 EO.
Table 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2 (Comparison)</th>
<th>3 (Comparison)</th>
<th>4 (Comparison)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-PH+5EO</td>
<td>5.0%</td>
<td>5.0%</td>
<td>5.0%</td>
<td>5.0%</td>
</tr>
<tr>
<td>Phosphated 2-PH+5EO</td>
<td>3.5%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphated C₉-C₁₁-alcohol +5.5EO</td>
<td></td>
<td>3.0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphated C₉-C₁₁-alcohol +4EO</td>
<td></td>
<td></td>
<td>3.4%</td>
<td></td>
</tr>
<tr>
<td>Phosphated 2-ethylhexanol +4EO</td>
<td></td>
<td></td>
<td></td>
<td>3.0%</td>
</tr>
<tr>
<td>Sodium metasilicate</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Tetrapotassium pyrophosphate</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Water</td>
<td>81.5</td>
<td>82.0</td>
<td>79.0</td>
<td>82.0</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Clarity interval (°C)</th>
<th>Appearance after dilution 1:5 after 1 day</th>
<th>Appearance after dilution 1:20 after 1 day</th>
<th>Appearance after dilution 1:5 after 1 week</th>
<th>Appearance after dilution 1:20 after 1 week</th>
<th>Soil removal at 1:20 dilution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0-70</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>Hazy but stable</td>
<td>60.0</td>
</tr>
<tr>
<td>2 (Comp.)</td>
<td>0-53</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>26.0</td>
</tr>
<tr>
<td>3 (Comp.)</td>
<td>0-60</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>44.0</td>
</tr>
<tr>
<td>4 (Comp.)</td>
<td>0-50</td>
<td>Hazy</td>
<td>Hazy</td>
<td>Cloudy</td>
<td>Hazy</td>
<td>54.0</td>
</tr>
</tbody>
</table>
The formulation according to the invention exhibited the best cleaning performance of all the investigated formulations, in combination with a good stability upon dilution.

Example 3
In this example the wetting ability of a composition according to the invention was measured by the modified Drave’s test.

<table>
<thead>
<tr>
<th>Table 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>Phosphated 2-PH+5EO</td>
</tr>
<tr>
<td>C₉-C₁₁-alcohol+4EO</td>
</tr>
<tr>
<td>Sodium nitrilotriacetate</td>
</tr>
</tbody>
</table>

In the modified Drave’s test, the sinking time in s is measured for a specified cotton yarn in approximately 0.1% surfactant solution. The formulation in the Table 5 was diluted with distilled water to 0.1% by weight with respect to the C₉-C₁₁-alcohol + 4 EO, and the modified Drave’s test was performed on this solution. The result is displayed in the Table 6, below.

<table>
<thead>
<tr>
<th>Table 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formulation</td>
</tr>
<tr>
<td>C</td>
</tr>
</tbody>
</table>

The formulation containing the phosphated 2-propylheptanol + 5 EO as a hydrotrope for the ethoxylate had a good wetting ability, whereas for the different components alone, the wetting time was >420 s. The C₉-C₁₁-alcohol is not soluble in this alkaline medium without a hydrotrope, and the phosphated 2-propylheptanol + 5 EO has no good wetting ability on its own. When the hydrotrope is added, the nonionic surfactant is solubilised, and it is then able to exert its wetting ability.
Example 4

In the syntheses described below a 1,000 cm³ flange flask equipped with an anchor stirrer was used. The reactor was heated by an electrical heater equipped with a thermostat. A slight flow of nitrogen was applied during the reaction. The polyphosphoric acid (PPA) used was Polyphosphoric acid 116, 84% equivalent in P₂O₅ (Albright & Wilson).

1) 2-propyleptanol + PPA
2-propyleptanol (222.47 g, 1.41 mole) was charged and heated to 45°C. PPA (254.09 g) was added from a 60 ml syringe and the exothermic reaction was kept at 55-70°C while stirring at 240 r/min. PPA was added during a period of 1 hour. The reaction was then left for 2 h at 60°C and with stirring at 300 r/min. After the post-reaction water (5.0 g) was added to hydrolyse the remaining PPA, after which the acid was neutralised with KOH (274.4 g) dissolved in 555.0 g water.

2) 2-propyleptanol + 3 EO +PPA
2-propyleptanol +3 EO (295.63 g, 1.02 mole) was charged and heated to 45°C. PPA (184.95 g) was added from a 60 ml syringe and the exothermic reaction was kept at 55-70°C while stirring at 240 r/min. PPA was added during a period of 1 hour. The reaction was then left for 2 h at 60°C and with stirring at 300 r/min. After the post-reaction water (5.0 g) was added to hydrolyse the remaining PPA, after which the acid was neutralised with KOH (191 g) dissolved in 454 g water.

3) 2-propyleptanol + 5 EO + PPA
2-propyleptanol + 5 EO (307.71 g, 0.81 mole) was charged and heated to 45°C. PPA (148 g) was added from a 60 ml syringe and the exothermic reaction was kept at 55-70°C while stirring at 240 r/min. PPA was added during a period of 1 hour. The reaction was then left for 2 h at 60°C and with stirring at 300 r/min. After the post reaction water (5.0 g) was added to hydrolyse the remaining PPA, after which 374.02 g acid were neutralised with KOH (132.37 g) dissolved in 517 g water.
Example 5

Morwet D-425 is a condensed alkyl naphthalene sulfonate dispersant commercially available from Akzo Nobel Surface Chemistry LLC, Chicago, IL, that has been used as the main dispersant in various pesticide suspension concentrate, wettable powder and water dispersible granule formulations. Frequently, a nonionic surfactant is used as a co surfactant to increase the wetting and stability of the formulations. Since the solubility of nonionic surfactants is decreased in the salt solution, flocculation will occur when pesticide formulation is mixed with fertilizer during application. This example is aimed to compare the performance of different co surfactant in Atrazine SC and to verify if the branched hydrophobe improves the compatibility in ammonium nitrate solution.

Materials

Atrazine Tech.
Morwet D-425 (condensed alkyl naphthalene sulfonate, sodium salt)
Ethylan 1005 phosphate ester (2-propyl heptanol + 5EO)
Emphos PS – 131 (iso-tridecanol + 6EO, phosphate ester, acid form)
Emphos PS-236 (linear C10/12 alcohol + 5EO, phosphate ester, acid form)
Witconol SN-70 (linear C10/12 alcohol + 5EO)
Witconol TD-60 (iso-tridecanol + 6EO)
Ethylan 1005 (2-propyl heptanol + 5EO)
Urea – ammonium nitrate

The Atrazine suspensions were made by first dissolving the Morwet D-425 and wetting agent in the appropriate volume of water. Micronized Atrazine technical was then added to the solution and then dispersed using high shear. All of the suspensions tested were made to contain 480 grams per liter of active ingredient.
After preparing the Atrazine suspensions with different surfactant systems, the suspensions were diluted into UAN and evaluated based on the degree of flocculation as a function of time.

**Formulations/Results/Observations**

<table>
<thead>
<tr>
<th></th>
<th>Atrazine (g)</th>
<th>D-425 (g)</th>
<th>Co surfactant (g)</th>
<th>Water (g)</th>
</tr>
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<tbody>
<tr>
<td>1996-17-1</td>
<td>8.4</td>
<td>1.0</td>
<td>0.4 (1005 phosphate ester)</td>
<td>10.2</td>
</tr>
<tr>
<td>1996-17-2</td>
<td>8.4</td>
<td>1.0</td>
<td>0.4 (PS-131)</td>
<td>10.2</td>
</tr>
<tr>
<td>1996-17-3</td>
<td>8.4</td>
<td>1.0</td>
<td>0.4 (TD-60)</td>
<td>10.2</td>
</tr>
<tr>
<td>1996-17-4</td>
<td>8.4</td>
<td>1.0</td>
<td>0.4 (Ethylan 1005)</td>
<td>10.2</td>
</tr>
<tr>
<td>1996-17-5</td>
<td>8.4</td>
<td>1.0</td>
<td>0.4 (PS-236)</td>
<td>10.2</td>
</tr>
<tr>
<td>1996-17-6</td>
<td>8.4</td>
<td>1.0</td>
<td>0.4 (SN-70)</td>
<td>10.2</td>
</tr>
<tr>
<td>1996-18-1</td>
<td>8.4</td>
<td>1.4</td>
<td>0.0</td>
<td>10.2</td>
</tr>
<tr>
<td>1996-18-2</td>
<td>8.4</td>
<td>1.0</td>
<td>0.0</td>
<td>10.6</td>
</tr>
<tr>
<td>1996-18-3</td>
<td>8.4</td>
<td>0.6</td>
<td>0.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Next, 5 mL of each sample were poured in 95 mL of UAN solutions in 100 mL tubes. The tubes were inverted 10 times and observed for flocculation. After sitting for 1, 2, 4, and 24 hours, the height of clear UAN solution from the bottom of tube was measured. The following results were found:

**Table 8. Atrazine formulation performance in UAN solution**

<table>
<thead>
<tr>
<th></th>
<th>1 hr (cm)</th>
<th>2 hr (cm)</th>
<th>4 hr (cm)</th>
<th>24 hr (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996-17-1</td>
<td>14.0</td>
<td>17.0</td>
<td>20.3</td>
<td>24.2</td>
</tr>
<tr>
<td>1996-17-2</td>
<td>22.5</td>
<td>23.3</td>
<td>24.4</td>
<td>25.7</td>
</tr>
<tr>
<td>1996-17-3</td>
<td>20.5</td>
<td>22.0</td>
<td>23.1</td>
<td>24.9</td>
</tr>
<tr>
<td>1996-17-4</td>
<td>19.0</td>
<td>20.0</td>
<td>21.1</td>
<td>22.7</td>
</tr>
<tr>
<td>Year</td>
<td>Value 1</td>
<td>Value 2</td>
<td>Value 3</td>
<td>Value 4</td>
</tr>
<tr>
<td>-------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>1996-17-5</td>
<td>22.5</td>
<td>23.7</td>
<td>24.6</td>
<td>26.1</td>
</tr>
<tr>
<td>1996-17-6</td>
<td>20.0</td>
<td>21.0</td>
<td>22.1</td>
<td>24.4</td>
</tr>
<tr>
<td>1996-18-1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>3.5</td>
</tr>
<tr>
<td>1996-18-2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.4</td>
<td>3.2</td>
</tr>
<tr>
<td>1996-18-3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Figure 1. Atrazine formulation performance in UAN solution

As seen above, all the cosurfactants decreased the SC compatibility in UAN solution because the salt precipitated the cosurfactant from the system. However, Ethylan 1005 phosphate ester (contained in sample 1996-17-1) did perform much better compared to other cosurfactants in the relatively short time period (up to 4 hr).

The difference in the results among formulations was significant enough to indicate that different hydrophobe lengths and branches can play an important role for compatibility issue.
Based on the data generated in this study, Ethylan 1005 phosphate ester showed the potential to improve the SC compatibility with UAN solution.
We claim

1. An agricultural formulation comprising at least one agricultural active, and at least one agricultural adjuvant, wherein said adjuvant comprises at least one phosphated 2-propylheptanol, phosphated 2-propylheptanol alkoxylate, or mixtures thereof.

2. The formulation of claim 1 wherein the alkoxylate on average comprises 1 to 20 ethyleneoxy units and 0-3 propyleneoxy and/or butyleneoxy units.

3. The formulation of claim 1 wherein the phosphated 2-propylheptanol or the phosphated 2-propylheptanol alkoxylate has the formula

\[
\text{H}_2\text{C}(-\text{CH}_2)_2\text{CH}(-\text{CH}_2\text{O})_c\text{CH}_2\text{O}(-\text{CH}_2\text{CH}_2\text{O})_n\text{P}(-\text{OM})_m\text{OM}
\]

(III)

wherein \( M \) is \( \text{H} \), a monovalent metal ion or \( R_1R_2R_3R_4\text{N}^+ \), where \( R_1, R_2, R_3, \) and \( R_4 \) are \( \text{H} \), an alkyl group with 1-4 carbon atoms or \(-\text{CH}_2\text{CH}_2\text{OH} \), and \( c \) is a number 0-20.

4. The formulation of claim 2 wherein the adjuvant comprises a mixture containing two or more of
- compounds of formula II,
- compounds of the formula

\[
\text{H}_2\text{C}(-\text{CH}_2)_2\text{CH}(-\text{CH}_2\text{O})_c\text{CH}_2\text{O}(-\text{CH}_2\text{CH}_2\text{O})_n\text{P}(-\text{OM})_m\text{OM}
\]

(III)

wherein \( n \) is 1-3 and \( M \) and \( c \) have the same meaning as in claim 3,
- compounds of the formula

\[
\text{H}_2\text{C}(-\text{CH}_2)_2\text{CH}(-\text{CH}_2\text{O})_c\text{CH}_2\text{O}(-\text{CH}_2\text{CH}_2\text{O})_n\text{P}(-\text{O}(-\text{CH}_2\text{CH}_2\text{O})_c\text{CH}_2\text{O}(-\text{CH}_2\text{CH}_2\text{O})_c\text{CH}_2\text{O}(-\text{CH}_2\text{CH}_2\text{O})_c\text{CH}_2\text{O})_m\text{OM}
\]

(IV)

wherein \( M \) and \( c \) have the same meaning as in claim 3, and
- compounds of the formula

\[
\text{H}_3\text{C}-(\text{CH}_2)_x\text{H}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_y\text{P}^\text{OM} \quad \text{OM} \quad \text{c} \quad \text{OM}
\]

(wherein M and c have the same meaning as in claim 3, and where c is present in an amount of at least 60% by weight of the adjuvant mixture.

5. The formulation of claim 1 wherein said phosphated 2-propylheptanol alkoxylate comprises 2 to 4 ethyleneoxy units.

6. The formulation of claim 5 wherein the phosphated alkoxylate comprises one or more products of the formulae

\[
\text{H}_3\text{C}-(\text{CH}_2)_x\text{H}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_y\text{P}^\text{OM} \quad \text{OM}
\]

(wherein M is H, a monovalent metal ion or R_1R_2R_3R_4N^+, where R_1, R_2, R_3, and R_4 are H, an alkyl group with 1-4 carbon atoms or -CH_2CH_2OH, and c is a number 2-4,

\[
\text{H}_3\text{C}-(\text{CH}_2)_x\text{H}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_y\text{P}^\text{OM} \quad \text{OM} \quad \text{c} \quad \text{OM}
\]

(wherein n is 1-3, M is H, a monovalent metal ion or R_1R_2R_3R_4N^+, where R_1, R_2, R_3, and R_4 are H, an alkyl group with 1-4 carbon atoms or -CH_2CH_2OH, and c is a number 0-20,

\[
\text{H}_3\text{C}-(\text{CH}_2)_x\text{H}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_y\text{P}^\text{OM} \quad \text{OM} \quad \text{c} \quad \text{OM}
\]

(wherein M and c have the same meaning as above, and
7. The agricultural formulation of claim 1 which comprises 0.1-30% by weight of said adjuvant that comprises phosphated 2-propylheptanol and/or a phosphated 2-propylheptanol alkoxylate, where the alkoxylate on average comprises 1 to 20 ethyleneoxy units and 0-3 propyleneoxy units.

8. The formulation of claim 7, wherein said adjuvant is a phosphated 2-propylheptanol alkoxylate comprising 2-4 ethyleneoxy units.

9. The formulation of claim 6 wherein in said one or more phosphated 2-propylheptanol alkoxylates having the formulae II, III, IV and/or V, the phosphated 2-propylheptanol alkoxylates having the formulae II is present in an amount of at least 80% by weight of the adjuvant mixture.

10. The formulation of claim 1 wherein said adjuvant is a dispersant, emulsifier, hydrotrope, wetting agent, and/or compatibility agent.

11. The formulation of claim 1 wherein said at least one agricultural active is a herbicide, fungicide, insecticide, plant growth regulator, or mixtures thereof.

11. A method of treating plants which comprises contacting said plants with an agriculturally effective amount of the agricultural formulation of claim 1.

12. An adjuvant for agricultural formulations, wherein said adjuvant comprises at least one phosphated 2-propylheptanol, phosphated 2-propylheptanol alkoxylate, or mixtures thereof.
13. The adjuvant of claim 12 wherein the alkoxyalkylamine on average comprises 1 to 20 ethyleneoxy units and 0-3 propylenoxy and/or butylenoxy units.

14. The adjuvant of claim 12 wherein the phosphated 2-propylheptanol or the phosphated 2-propylheptanol alkoxyalkylamine has the formula

\[
\text{H}_3\text{C}-(\text{CH}_2)_4\text{CH}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})^c\text{P}^\text{OM} \quad (\text{II})
\]

where M is H, a monovalent metal ion or R_1R_2R_3R_4N^+, where R_1, R_2, R_3, and R_4 are H, an alkyl group with 1-4 carbon atoms or -\text{CH}_2\text{CH}_2\text{OH}, and c is a number 0-20.

15. The formulation of claim 14 wherein the adjuvant comprises a mixture containing two or more of
- compounds of formula II,
- compounds of the formula

\[
\text{H}_3\text{C}-(\text{CH}_2)_4\text{CH}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})^c\text{P}^\text{OM} \quad (\text{III})
\]

wherein n is 1-3 and M and c have the same meaning as in claim 3,
- compounds of the formula

\[
\text{H}_3\text{C}-(\text{CH}_2)_4\text{CH}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})^c\text{P}^\text{OM} \quad (\text{IV})
\]

wherein M and c have the same meaning as in claim 3, and
- compounds of the formula

\[
\text{H}_3\text{C}-(\text{CH}_2)_4\text{CH}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})^c\text{P}^\text{OM} \quad (\text{V})
\]

wherein M and c have the same meaning as in claim 3, and where II is present in an amount of at least 60% by weight of the adjuvant mixture.
16. The formulation of claim 12 wherein said phosphated 2-propylheptanol alkoxylate comprises 2 to 4 ethyleneoxy units.

17. The formulation of claim 16 wherein the phosphated alkoxylate comprises one or more products of the formulae

$$\text{H}_3\text{C}-(\text{CH}_2)_4\text{CH}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_c\text{P}^{\text{OM}}$$

(II)

wherein M is H, a monovalent metal ion or R_1R_2R_3R_4N^+, where R_1, R_2, R_3, and R_4 are H, an alkyl group with 1-4 carbon atoms or –CH_2CH_2OH, and c is a number 2-4,

$$\text{H}_3\text{C}-(\text{CH}_2)_4\text{CH}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{P}^{\text{OM}}$$

(III)

wherein n is 1-3, M is H, a monovalent metal ion or R_1R_2R_3R_4N^+, where R_1, R_2, R_3, and R_4 are H, an alkyl group with 1-4 carbon atoms or –CH_2CH_2OH, and c is a number 0-20,

$$\text{H}_3\text{C}-(\text{CH}_2)_4\text{CH}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_c\text{P}^{\text{OM}}-(\text{CH}_2\text{CH}_2\text{O})_c\text{P}^{\text{OM}}$$

(IV)

wherein M and c have the same meaning as above, and

$$\text{H}_3\text{C}-(\text{CH}_2)_4\text{CH}-\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_c\text{P}^{\text{OM}}-(\text{CH}_2\text{CH}_2\text{O})_c\text{P}^{\text{OM}}\text{CH}_3$$

(V)

wherein M and c have the same meaning as above.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

**IPC** 7 A01N25/30 C07F9/09

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

**IPC** 7 A01N C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>X</td>
<td>EP 0 256 427 A (HOECHST AKTIENGESELLSCHAFT) 24 February 1988 (1988-02-24) page 3, line 17 - line 22; claims</td>
<td>1-10, 12-17</td>
</tr>
<tr>
<td>X</td>
<td>CH 481 953 A (STAUFFER CHEMICAL COMPANY) 30 November 1969 (1969-11-30) column 4, line 46 - column 5, line 15</td>
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<tr>
<td>A</td>
<td>GB 2 049 427 A (MONSANTO CO) 31 December 1980 (1980-12-31) page 2, line 65 - page 3, line 5; claims</td>
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<td>A</td>
<td>US 4 975 110 A (PURITCH ET AL) 4 December 1990 (1990-12-04) claims</td>
<td>1-17</td>
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</table>

**X** Further documents are listed in the continuation of box C. **X** Patent family members are listed in annex.

* Special categories of cited documents:
  * "A" document defining the general state of the art which is not considered to be of particular relevance
  * "E" earlier document but published on or after the international filing date
  * "L" document containing new content relating to the subject matter of the invention
  * "O" document referring to an oral disclosure, use, exhibition or other means
  * "P" document published prior to the international filing date but later than the priority date claimed
  * "S" later document published after the international filing date or priority date and set in conflict with the application but cited to understand the principle or theory underlying the invention
  * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  * "Y" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  * "Z" document member of the same family

**Date of the actual completion of the International Search**

14 October 2005

**Date of mailing of the international search report**

03/11/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HT Rijswijk, Tel: (+31-70) 540-2000, Tc: 31 651 eep nl, Fax: (+31-70) 540-2016

Authorized officer

Pfannenstiel, H
<table>
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<th>Relevant to claim No.</th>
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| A        | US 6 432 884 B1 (LACHUT FRANK J)  
13 August 2002 (2002-08-13)  
claims | 1-17                              |
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<th>Publication date</th>
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<th>Publication date</th>
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<tr>
<td></td>
<td></td>
<td>JP 2804935 B2</td>
<td>30-09-1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 63051934 A</td>
<td>05-03-1988</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 4986851 A</td>
<td>22-01-1991</td>
</tr>
<tr>
<td>CH 481953 A</td>
<td>30-11-1969</td>
<td>BE 705984 A</td>
<td>30-04-1968</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 1142425 A</td>
<td>05-02-1969</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL 6714652 A</td>
<td>05-11-1968</td>
</tr>
<tr>
<td>GB 2049427 A</td>
<td>31-12-1980</td>
<td>CA 1170856 A1</td>
<td>17-07-1984</td>
</tr>
<tr>
<td>US 4975110 A</td>
<td>04-12-1990</td>
<td>AT 176380 T</td>
<td>15-02-1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2067773 A1</td>
<td>14-04-1991</td>
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<tr>
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<td>DE 69032940 D1</td>
<td>18-03-1999</td>
</tr>
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</tr>
<tr>
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<td></td>
<td>JP 5502216 T</td>
<td>22-04-1993</td>
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Form PCT/SA/10 (patent family entries) (January 2004)