

关于2-吡啶偶氮试剂的进展

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关于2-吡啶偶氮试剂的发展

2-吡啶偶氮化合物在化学分析方面的应用是在近十年来才被进一步广泛研究的。其中以1-(2-吡啶偶氮)-2-萘酚(PAN)和2-(2-吡啶偶氮)-间苯二酚(PAR)为代表的,在测试金属上是多方面应用的试剂,同时也是杰出的金属变色指示剂。它可以测定30种以上的元素,尤其在微量分析上PAN和PAR用途更为广泛,这些试剂在光度测定上对某些金属有很高的灵敏度。

2-吡啶偶氮试剂在分析上的应用,主要是用在光度测定和金属络合滴定上成为这方面很有前途的特效试剂门类之一。其他也可作为沉淀法和萃取滴定,光度萃取剂,氧化试剂及点滴试剂中的指示剂。

一般用2-吡啶偶氮化合物作为发色剂时要与萃取技术相结合,有所谓不同的方法:①将吡啶偶氮试剂做水溶液与水相,再经有机相中反萃,用水相作光度测定。②先将金属萃取于水溶液中,藉加适当的有机萃取剂为有机相,再将偶氮试剂加于有机相中进行光度比色。

由于2-吡啶偶氮化合物与被测金属离子络合时, H^+ 离子和其他金属离子而争夺,因此要在低pH值和金属络合稳定性高的情况下才做有效。所以在测定中要选择适宜的pH值遮蔽剂和萃取剂才能提高它的选择性。

当前国外对这类试剂的报导迅速增多,已对50余种进行了研究和应用。其品名我们按结构分列列表(见后附表)仅供参考。

我们目前对这类试剂研究和生产作的很少,曾对PADAP的衍生物(5-Br-PADAP)合成和测试作了工作。该试剂是测定低含量铀的高灵敏度试剂。 UO_2^{4+} -Br-PADAP络合物在 $\lambda = 578m\mu$ pH=7.6时充分吸收系数是2000。在混合络合物溶液存在时只有 Cr^{+3} , V^{+5} , Pb^{+2} 严重干扰。用70%二次萃取后(三辛基氧膦)在有机相中直接显色(以前用传统的偶氮胂法要经过三次萃取才能显色,因此,提供了分光光度法测定各种材料中铀高灵敏、高选择的好方法。用该试剂测低含量的铀时,具有很好的准确度、精密度及简单、快速的优点,该产品经有关单位使用反映良好。此外我们对该试剂合成上作了改进,在络合上用冰醋酸代替 CO_2 ,再从HCl水溶液中析出的方法,突破了国外对2-吡啶偶氮试剂在络合时用 CO_2 传统的方法,手续简单稳定,产品收率提高约30%产量,灵敏度均高于文献报导,为合成2-吡啶偶氮试剂系列物创造了有利的条件。

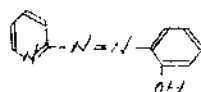
附表 I)

57种 2-吡啶基偶氮试剂:

2 Pyridylazo Reagents.

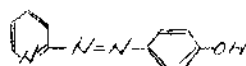
1. 邻-(2-吡啶偶氮)苯酚

O-(2-Pyridylazo) phenol
O-PAP



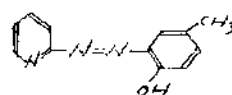
2. 对-(2-吡啶偶氮)苯酚

P-(2-Pyridylazo) phenol
P-PAP



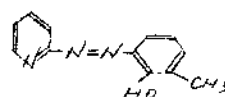
3. 2-(2-吡啶偶氮)-对-甲酚

2-(2-Pyridylazo)-p-cresol
PAC



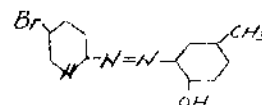
4. 6-(2-吡啶偶氮)-邻-甲酚

6-(2-Pyridylazo)-O-cresol
O-PAC



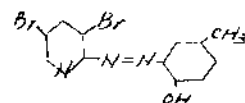
5. 2-[(5-溴-2-吡啶)偶氮]-对-甲酚

2-[(5-Bromo-2-pyridyl)azo]-p-cresol
5-bromo-PAC



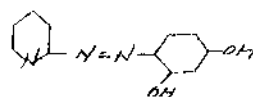
6. 2-[(3,5-二溴-2-吡啶)偶氮]-对-甲酚

2-[(3,5-Dibromo-2-pyridyl)azo]-p-cresol



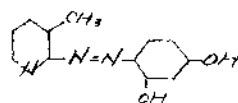
7. 4-(2-吡啶偶氮)间苯二酚

4-(2-Pyridylazo) resorcinol
PAR



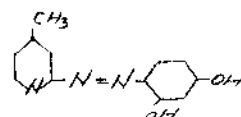
8. 4-[(3-甲基-2-吡啶)偶氮]间苯二酚

4-[(3-Methyl-2-pyridyl)azo] resorcinol
3-Methyl-PAR



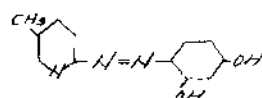
9. 4-[(4-甲基-2-吡啶)偶氮]间苯二酚

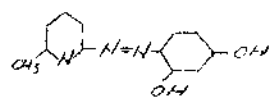
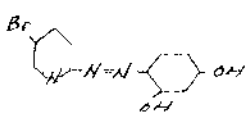
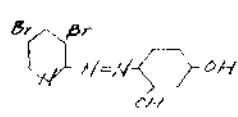
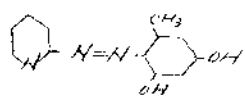
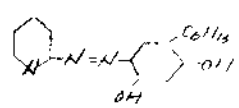
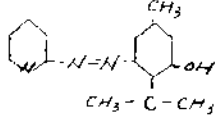
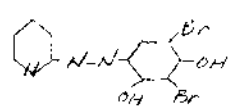
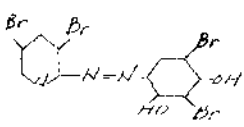
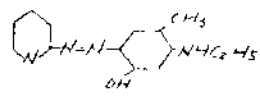
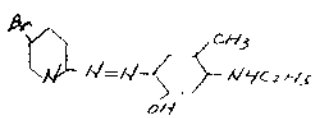
4-[(4-Methyl-2-pyridyl)azo] resorcinol
4-Methyl-PAR



10. 4-[(5-甲基-2-吡啶)偶氮]间苯二酚

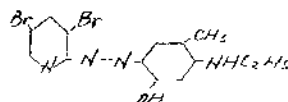
4-[(5-Methyl-2-pyridyl)azo]-resorcinol
5-Methyl-PAR



11. 4-[(6-甲基-2-吡啶)偶氮]-间苯二酚
4-[(6-Methyl-2-pyridyl)azo]-resorcinol
6-Methyl-PAR 
12. 4-[(5-溴-2-吡啶)偶氮]-间苯二酚
4-[(5-Bromo-2-pyridyl)azo]-resorcinol
5-bromo-PAR 
13. 4-[(3,5-二溴-2-吡啶)偶氮]-间苯二酚
4-[(3,5-Dibromo-2-pyridyl)azo]-resorcinol
3,5-dibromo-PAR 
14. 4-(2-吡啶偶氮)苦黑酚
4-(2-pyridylazo) orcinol (PAO)
5-Methyl-4-(2-pyridylazo)resorcinol 
15. 4-己基-6-(2-吡啶偶氮)-间苯二酚
4-Hexyl-6-(2-pyridylazo)-resorcinol
PAR-4-hexyl 
16. 5-(2-吡啶偶氮)百里酚
5-(2-pyridylazo)thyniol
PAT 
17. 2,6-二溴-4-(2-吡啶偶氮)-间苯二酚
2,6-Dibromo-4-(2-pyridylazo)resorcinol
PAR-2,6-dibromo 
18. 2,6-二溴-4-[(3,5-二溴-2-吡啶)偶氮]-间苯二酚
2,6-Dibromo-4-[(3,5-dibromo-2-pyridyl)azo]resorcinol
tetrabromo-PAR 
19. 5-(乙氨基)-2-(2-吡啶偶氮)-对-甲酚
5-(Ethylamino)-2-(2-pyridylazo)-p.cresol
PAAC, EAPAC* 
20. 2-[(5-溴-2-吡啶偶氮)]-5-(乙氨基)-对-甲酚
2-[(5-Bromo-2-pyridyl)azo]-5-(ethylamino)-p.cresol
5-dibromo-PAAC, 5-dibromo-EAPAC* 

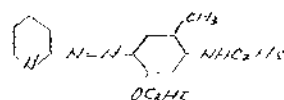
21. 2-[3,5-二溴-2-吡啶)偶氮]-5-(乙氨基)-对-甲酚

2-[3,5-Dibromo-2-pyridylazo]-5-(ethylamino)-p-cresol
3,5-dibromo-PAAC;
3,5-dibromo-EAPAC*



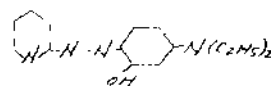
22. 11-乙基-6-甲基-4-(2-吡啶偶氮)间-乙基苯胺

11-Ethyl-6-methyl-4-(2-Pyridylazo)-M-phenetidine
EMAP-EMPHAT*



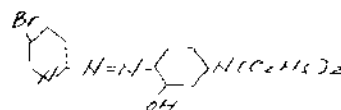
23. 5-(二乙氨基)-2-(2-吡啶偶氮)-苯酚

5-(Diethylamino)-2-(2-Pyridylazo)-phenol
PAAP-DEPA*



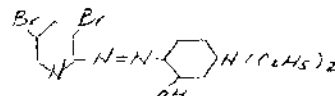
24. 2-[5-溴-2-吡啶)偶氮]-5-(二乙氨基)苯酚

2-[5-Bromo-2-pyridylazo]-5-(diethylamino)phenol
5-bromo-PAAP,
5-bromo-DEPA*



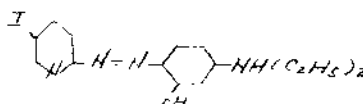
25. 2-[3,5-二溴-2-吡啶)偶氮]-5-(二乙氨基)苯酚

2-[3,5-Dibromo-2-pyridylazo]-5-(Diethylamino)phenol
3,5-dibromo-PAAP,
3,5-dibromo-DEPA*



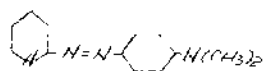
26. 5-(二乙氨基)-2-[5-碘-2-吡啶)偶氮]苯酚

5-(Diethylamino)-2-[5-iodo-2-pyridylazo]phenol
5-iodo-PAAP,
5-iodo-DEPA*



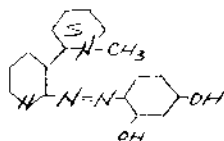
27. *N,N*-二甲-对-(2-吡啶偶氮)苯胺

N,N-Dimethyl-*p*-(2-pyridylazo)aniline
PADA·PAA DNIPAA*



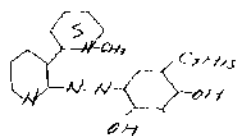
28. 4-[[3-(1-甲基-2-哌啶)-2-吡啶]偶氮]间苯二酚

4-[[3-(1-Methyl-2-piperidyl)-2-pyridyl]resorcinol



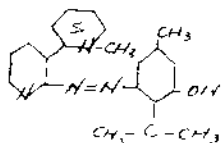
29. 4-庚基-6-[[3-(1-甲基-2-哌啶)-2-吡啶]偶氮]间苯二酚

4-Heptyl-6-[[3-(1-Methyl-2-piperidyl)-2-pyridyl]azo]resorcinol
MPPAR-4-heptyl



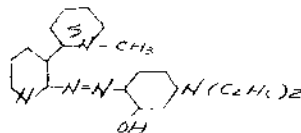
30. 5-[[3-(1-甲基-2-哌啶基)-2-吡啶]偶氮]百里酚

5-[[3-(1-Methyl-2-piperidyl)-2-pyridyl]azo]thymol
MPPAT



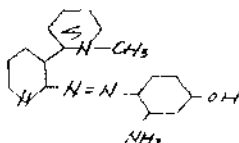
31. 5-(二乙氨基)-2-[[3-(1-甲基-2-哌啶)-2-吡啶]偶氮]苯酚

5-(Diethylamino)-2-[[3-Methyl-1,2-piperidyl)-2-pyridyl]azo]phenol
DMPPP, DemppA*



32. 3-氨基-4-[[3-(1-甲基-2-哌啶)-2-吡啶]偶氮]苯酚

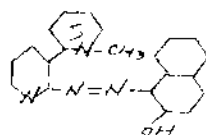
3-Amino-4-[[3-(1-Methyl-2-piperidyl)-2-pyridyl]azo]phenol
AMPPAP



33. 1-[(3-(1-甲基-2-吡啶)-2-吡啶)偶氮]-2-萘酚

1-[(3-(1-Methyl-2-piperidyl)-2-pyridyl)azo]-2-Naphthol

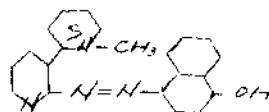
MAAN; MIPAN*



34. 4-[(3-(1-甲基-2-吡啶)-2-吡啶)偶氮]-1-萘酚

4-[(3-(1-Methyl-2-piperidyl)-2-pyridyl)azo]-1-Naphthol

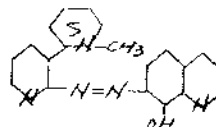
P-MAAN; P-MPPN*



35. 7-[3-(1-甲基-2-吡啶)-2-吡啶]偶氮-8-羟基喹啉

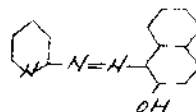
7-[3-(1-Methyl-2-piperidyl)-2-pyridyl]azo]-8-quinolinol

MAAOx, MPPAOx



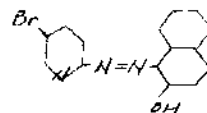
36. 1-(2-吡啶偶氮)-2-萘酚

1-(2-pyridylazo)-2-Naphthol
PAN; B-PAN



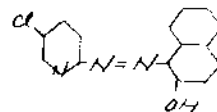
37. 1-[(5-溴-2-吡啶)偶氮]-2-萘酚

1-[(5-Bromo-2-pyridyl)azo]-2-Naphthol
5-bromo-PAN



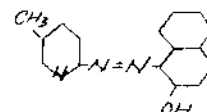
38. 1-[(5-氯-2-吡啶)偶氮]-2-萘酚

1-[(5-Chloro-2-pyridyl)azo]-2-Naphthol
5-chloro-PAN



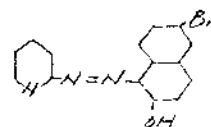
39. 1-[(5-甲基-2-吡啶)偶氮]-2-萘酚

1-[(5-Methyl-2-pyridyl)azo]-2-Naphthol
5-Methyl-PAN



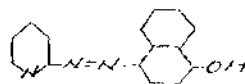
40. 6-溴-1-(2-吡啶偶氮)-2-萘酚

6-Bromo-1-(2-Pyridylazo)-2-Naphthol
PAN-6-Br



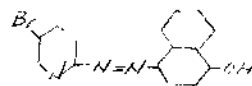
41. 4-(2-吡啶偶氮)-1-萘酚

4-(2-pyridylazo)-1-Naphthol
P-PAN



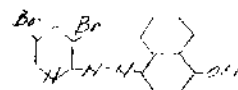
42. 4-[(5-溴-2-吡啶)偶氮]-1-萘酚

4-[(5-Bromo-2-pyridyl)azo]-1-Naphthol
5-bromo-p-PAN



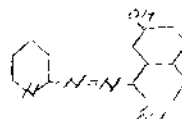
43. 4-[3,5-二溴-2-吡啶)偶氮]-1-萘酚

4-[3,5-Dibromo-2-pyridyl)azo]-1-Naphthol
3,5-dibromo-p-PAN



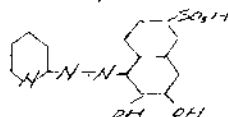
44. 1-(2-吡啶偶氮)-2,7-萘二酚

1-(2-Pyridylazo)-2,7-Na, tholenediol
2,7-PADN, 2,7-PAN



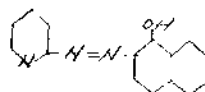
45. 6,7-二羟基-5-(2-吡啶偶氮)-2-萘磺酸

6,7-Dihydroxy-5-(2-pyridylazo)-2-Naphthalene sulfonic acid
PADNS



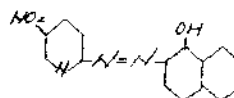
46. 2-(2-吡啶偶氮)-1-萘酚

2-(2-Pyridylazo)-1-Naphthol
2-PAN



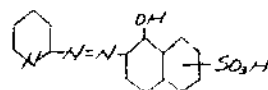
47. 2-[(5-硝基-2-吡啶)偶氮]-1-萘酚

2-[(5-Nitro-2-pyridyl)azo]-1-Naphthol
5-Nitro-2-PAN



48. 2-(2-吡啶偶氮)-1-萘酚-X-磺酸

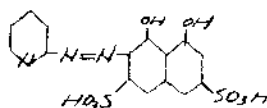
2-(2-pyridylazo)-1-Naphthol-X-sulfonic acid
(X=4,5,6,7 or 8) 2-PAN-X-S



49. 4,5-二羟基-3-(2-吡啶偶氮)-2,7-萘二磺酸

4,5-Dihydroxy-3-(2-pyridylazo)-2,7-Naphthalene disulfonic acid
(2-pyridylazo) chromotropic acid)

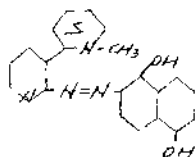
PACH



10. 2-[(3-(1-甲基-2-吡啶)-2-吡啶)偶氮]-1,5-萘二酚

2-[(3-(1-Methyl-2-pyridyl)-2-pyridyl]azo-1,5-Naphthalene-diol

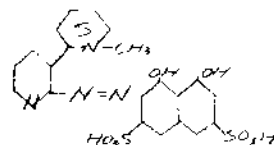
MP1, 5 PADN



11. 4,5-二羟基-3-[(3-(1-甲基-2-吡啶)-2-吡啶)偶氮]-2,7-萘二磺酸

4,5-Dihydroxy-3-[(3-(1-Methyl-2-pyridyl)-2-pyridyl]azo-2,7-Naphthalene disulfonic acid

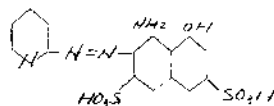
MPPACH



12. 4-氨基-5-羟基-3-(2-吡啶偶氮)-2,7-萘二磺酸

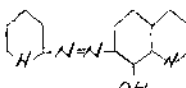
4-Amino-5-Hydroxy-3-(2-pyridylazo)-2,7-Naphthalene disulfonic acid (2-pyridylazo)-H-acid

PA-H; PAH



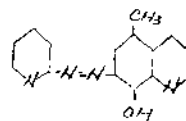
13. 7-(2-吡啶偶氮)-8-喹啉醇

7-(2-Pyridylazo)-8-quinolinol



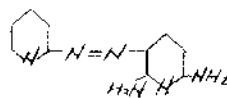
14. 5-甲基-7-(2-吡啶偶氮)-8-喹啉醇

5-Methyl-7-(2-pyridylazo)-8-quinolinol
PAOx-5-Methyl



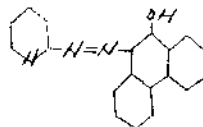
15. 2,6-二氨基-3-(吡啶偶氮)吡啶

2,6-Diamino-3-(pyridylazo)pyridine
DAPAPY



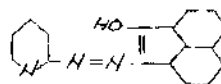
16. 10-(2-吡啶偶氮)-9-菲酚

10-(2-Pyridylazo)-9-phenanthrol
PAPH; PAPHen



17. 2-(吡啶偶氮)-1-萘醇

2-(Pyridylazo)-1-acenaphthylene
PAAC; PAACn



附表 II

4.3 种业经研究使用的品种:

2-Pyridylazo Compounds

- 1-(2-吡啶偶氮)-2-萘酚
- 1-(2-Pyridylazo)-2-Naphthol (PAN)
- 4-(2-吡啶偶氮)-1-萘酚
- 4-(2-Pyridylazo)-1-Naphthol (p-PAN)
- 2-(2-吡啶偶氮)-1-萘酚
- 2-(2-Pyridylazo)-1-Naphthol (2 PAN)
- 2-[(5-硝基-2-吡啶)偶氮]-1-萘酚
- 2-[(5-Nitro-2-pyridyl)azo]-1-Naphthol (5-Nitro-2 PAN)
- 4-(2-吡啶偶氮)间苯二酚
- 4-(2-Pyridylazo) resorcinol (PAR)
- 2-(2-吡啶偶氮)-对-甲酚
- 2-(2-Pyridylazo)-p-Cresol (PAC)
- 2-[(5-溴-2-吡啶)偶氮]-对-甲酚
- 2-[(5-Bromo-2-pyridyl)azo]-p-Cresol (5-bromo-PAC)
- 4-[(5-溴-2-吡啶)偶氮]间苯二酚
- 4-[(5-Bromo-2-pyridyl)azo]-resorcinol
- 4-[(3,5-二溴-2-吡啶)偶氮]间苯二酚
- 4-[(3,5-Dibromo-2-pyridyl)azo]-resorcinol
- 4-己基-6-(2-吡啶偶氮)间苯二酚
- 4-Hexyl-6-(2-Pyridylazo) resorcinol
- 2,6-二溴-4-(2-吡啶偶氮)间苯二酚
- 2,6-Dibromo-4-(2-pyridylazo) resorcinol
- 2,6-二溴-4-(3,5-二溴-2-吡啶)偶氮]间苯二酚
- 2,6-Dibromo-4-[(3,5-Dibromo-2-pyridyl)azo] resorcinol
- 邻-(2-吡啶偶氮)苯酚
- O-(2-pyridylazo) phenol (O-PAP)
- 对-(2-吡啶偶氮)苯酚
- p-(2-Pyridylazo) phenol (P-PAP)
- 4-(2-吡啶偶氮)苦黑酚
- 4-(2-Pyridylazo) orcinol (PAO)

- 5- (2-氨基)-2- (2-吡啶偶氮)-对-甲酚
- 5- (Diethylamino)-2- (2-Pyridylazo)-p-Cresol (EAPAC)
- 11- (2-氨基)-2- (2-吡啶偶氮)-间-乙氧基苯胺
- 1-Ethyl-4-Methyl-4- (2-Pyridylazo)-M-phenetidine (EMPAnt)
- 5- (2-氨基)-2- (2-吡啶偶氮) 苯酚
- 5- (Diethylamino)-2- (2-Pyridylazo) phenol (DEPA10)
- 2- (2-氨基)-2- (2-吡啶偶氮)-1-萘酚
- 4- (5-Bromo-2-Pyridylazo)-1-Naphthol (5-Bromo-p-PAN)
- 4- (3,5-二溴-2-吡啶偶氮)-1-萘酚
- 4- (3,5-二溴-2-pyridylazo)-1-Naphthol (3,5-Dibromo-p-PAN)
- 2- (2-氨基偶氮)-1-萘酚-X-磺酸
- 2- (2-Pyridylazo)-1-Naphthol-X-Sulfonic acid (2-PAN-X-S)
- 2- (2-氨基偶氮) 萘磺酸
Hydroxy (2-Pyridylazo) Naphthalene sulfonic acid
(2-氨基)-2- (2-吡啶偶氮)-2-萘酚
- 1- (5-Bromo-2-Pyridylazo)-2-Naphthol (5-bromo-PAN)
- 2-溴-1- (2-氨基偶氮)-2-萘酚
- 1-Bromo-1- (2-Pyridylazo)-2-Naphthol (PAN-6-Br)
- 1- { [3- (1-甲基-2-吡啶)-2-吡啶] 偶氮 } 间苯二酚
- 4- { [3- (1-Methyl-2-piperidyl)-2-Pyridyl] azo } resorcinol (MPPAN)
- 4-氨基-6- { [3- (1-甲基-2-吡啶)-2-吡啶] 偶氮 } 间苯二酚
- 4-Hyptyl-6- { [3- (1-Methyl-2-piperidyl)-2-Pyridyl] azo } resorcinol (MPPAN-4-Hyptyl)
- 3- (2-氨基偶氮) 百里酚
- 3- (2-Pyridylazo) thymol (PAT)
- 1- { [3- (1-甲基-2-吡啶)-2-吡啶] 偶氮 } 百里酚
- 5- { [3- (1-Methyl-2-piperidyl)-2-Pyridyl] azo } thymol (MPPAT)
- 2- { [3- (1-甲基-2-吡啶)-2-吡啶] 偶氮 }-1-萘酚
- 2- { [3- (1-Methyl-2-piperidyl)-2-Pyridyl] azo }-1-Naphthol (p-MPPAN)
- 5- (2-氨基)-2- { [3- (1-甲基-2-吡啶)-2-吡啶] 偶氮 } 苯酚
- 5- (Diethylamino)-2- { [3- (1-Methyl-2-piperidyl)-2-Pyridyl] azo } phenol

(DEMPPAP)

3-氨基-4-{[3-(1-甲基-2-吡啶)-2-吡啶]偶氮}苯酚

3-Amino-4-{[3-(1-Methyl-2-piperidyl)-2-pyridyl]azo}phenol
(AMPPAP)

1-(2-吡啶)-2,7-萘二酚

1-(2-Pyridylazo)-2,7-Naphthalenediol (2,7-PADN)

6,7-二羟基-5-(2-吡啶偶氮)-2-萘磺酸

6,7-Dihydroxy-5-(2-pyridylazo)-2-Naphthalene sulfonic acid
(PADNS)

4,5-二羟基-3-(2-吡啶偶氮)-2,7-萘二磺酸

4,5-Dihydroxy-3-(2-pyridylazo)-2,7-Naphthalene disulfonic acid
(PACH)

4-氨基-5-羟基-3-(2-吡啶偶氮)-2,7-萘二磺酸

4-Amino-5-Hydroxy-3-(2-pyridylazo)-2,7-Naphthalene disulfonic
acid

(PACH)

4-氨基-5-羟基-3-(2-吡啶偶氮)-2,7-萘二磺酸

4-Amino-5-hydroxy-3-(2-pyridylazo)-2,7-Naphthalene disulfonic
acid

(PA-H)

2-{[3-(1-甲基-2-吡啶)-2-吡啶]偶氮}-1,5-萘二酚

2-{[3-(1-Methyl-2-piperidyl)-2-pyridyl]azo}-1,5-Naphtha-
lenediol

(MP-1,3-PADN)

4,5-二羟基-3-{[3-(1-甲基-2-吡啶)-2-吡啶]偶氮}-9-萘二磺酸

4,5-Dihydroxy-3-{[3-(1-Methyl-2-piperidyl)-2-pyridyl]azo}-9-
Naphthalene disulfonic acid (MPPACH)

10-(2-吡啶偶氮)-9-菲酚

10-(2-pyridylazo)-9-phenanthrol (PAPH)

2-(2-吡啶偶氮)-萘醇

2-(2-pyridylazo)-acenaphthylenol (PAAC)

7-(2-吡啶偶氮)-8-醌醇

7-(2-Pyridylazo)-8-quinolinal (PAOX)

N,N-二甲基-对-(2-吡啶偶氮)苯胺

N,N-Dimethyl-p-(2-pyridylazo)aniline (DMPAA)

2,6-二氨基-3-(吡啶偶氮)吡啶

2,6-Diamino-3-(Pyridylazo)pyridine (DAPAY)