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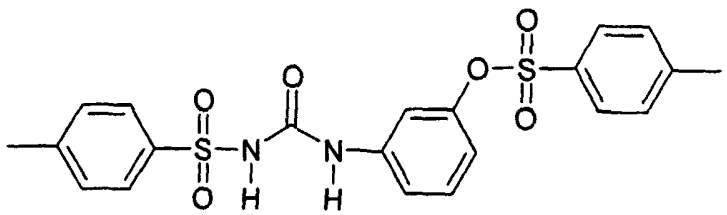
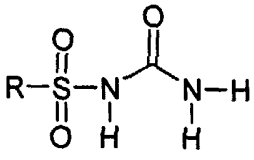
(54) Title: MIXTURE OF COLOUR DEVELOPERS



(I)



(II)

(57) Abstract: Mixture of colour developers comprising a compound of the formula (I) and a compound of formula (II), wherein R^1 is C_1-C_{20}alkyl or C_6-C_{10}aryl, which can be substituted one to three times with halogen, C_1-C_4alkyl, -NR^2R^3, wherein R^2 and R^3 independently from each other stand for hydrogen or C_1-C_8alkyl, or C_1-C_8acyl amino, a heat sensitive recording and the use of the inventive mixture for the manufacture of a heat-sensitive colored image-forming layer for the manufacture of heat-sensitive recording material.

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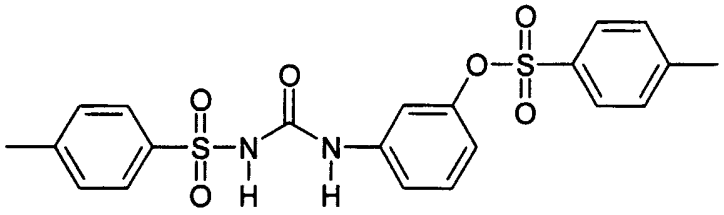
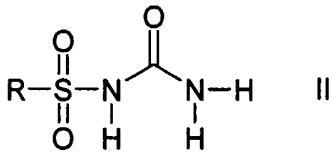
Mixture Of Colour Developers

The present invention relates to a mixture of colour developers comprising a compound of the formula I



I

and a compound of formula II



II

wherein

R^1 is C_1-C_{20}alkyl or C_6-C_{10}aryl, which can be substituted one to three times with halogen, C_1-C_4alkyl, -NR^2R^3, wherein R^2 and R^3 independently from each other stand for hydrogen or C_1-C_8alkyl, or C_1-C_8acyl amino, and their use in heat sensitive compositions.

Compound I is disclosed in EP-A 1,140,515. Though this compound exhibits excellent properties with regard to resistance to plasticiser, oil and heat ageing and a very good background whiteness, still a need exists to even further improve background whiteness, in particular after ageing at elevated temperature in a humid atmosphere, and to improve image whilst showing at least equal properties with regard to initial image density and resistance to oil compared to compound I.

Accordingly, the claimed composition has been found. In addition, a heat sensitive recording material has been found, too, as well as the use of the claimed mixture in heat sensitive recording materials.

Compounds I and II are commercially available or can be synthesized according to known methods (see e.g. EP-A 1,140,515).

In a preferred embodiment of this invention the weight ratio of compounds I and II are chosen in the range of from 999:1 to 1:1, preferably from 999:1 to 3:1.

C_1-C_{20}alkyl stands for branched or unbranched C_1-C_{20}alkyl such as e.g. for methyl, ethyl, n-, i-propyl, n-, i-, sec.-, tert.-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-eicosyl, preferably for C_1-C_8alkyl such as methyl, ethyl, n-, i-propyl, n-, i-, sec.-, tert.-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, more preferably for C_1-C_4alkyl such as methyl, ethyl, n-, i-propyl, n-, i-, sec.-, tert.-butyl.

C_1-C_8acyl amino stands for –NH-C(=O)-C_1-C_8alkyl, preferably for -NH-C(=O)-CH_3, -NH-C(=O)-C_2H_5, -NH-C(=O)-n-Pr, -NH-C(=O)-i-Pr, -NH-C(=O)-n-Bu, -NH-C(=O)-i-Bu, -NH-C(=O)-sec.-Bu, or -NH-C(=O)-tert.-Bu.

C_6-C_{10}aryl stands for phenyl or naphthyl. Preferred substituted C_6-C_{10}aryl groups are tolyl, xylenyl, anisoyl.

Halogen stands for fluorine, chlorine, bromine or iodine, preferably for chlorine, bromine.

In a preferred embodiment $-NR^2R^3$ stands for dimethylamino, diethylamino, diphenylamino or dibenzylamino.

In a preferred embodiment R^1 stands for hexadecyl, phenyl, 4-methyl phenyl, or naphthyl.

Another preferred embodiment of this invention relates to a heat sensitive recording material comprising:

a) a substrate sheet, and

b) a heat sensitive colored image-forming layer formed on the surface of the substrate sheet and comprising

b1) a colour former compound

b2) the inventive mixture of colour developers.

Usually the components b1) and b2) are used in a weight ratio in the range of from 1:1 to 5:1, preferably from 2:1 to 3:1.

As colour former compounds the known colour former compounds can be used, which are, as a rule, based on derivatives of, for example, triphenylmethanes, lactones, benzoxazines, spiropyrans or preferably fluorans.

Preferred colour formers include, but are not limited to: 3-diethylamino-6-methylfluoran, 3-dimethylamino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-(2,4-dimethylanilino) fluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-6-methyl-7-(3-trifluoromethylanilino) fluoran, 3-diethylamino-6-methyl-7-(2-chloroanilino) fluoran, 3-diethylamino-6-methyl-7-(4-chloroanilino) fluoran, 3-diethylamino-6-methyl-7-(2-fluoroanilino) fluoran, 3-diethylamino-6-methyl-7-(4-n-octylanilino) fluoran, 3-diethylamino -7-(4-n-octylanilino) fluoran, 3-diethylamino -7-(n-octylamino) fluoran, 3-diethylamino -7-(dibenzylamino) fluoran, 3-diethylamino-6-methyl-7-(dibenzylamino) fluoran, 3-diethylamino-6-chloro-7-methylfluoran, 3-diethylamino-7-t-butylfluoran, 3-diethylamino -7-carboxyethylfluoran, 3-diethylamino-6-chloro-7-anilinofluoran, 3-diethylamino-6-methyl-7-(3-methylanilino) fluoran, 3-diethylamino-6-methyl-7-(4-methylanilino) fluoran, 3-diethylamino-6-ethoxyethyl-7-anilinofluoran, 3-diethylamino-7-methylfluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-7-(3-trifluoromethylanilino) fluoran, 3-diethylamino-7-(2-chloroanilino) fluoran, 3-

diethylamino-7-(2-fluoroanilino) fluoran, 3-diethylamino-benzo[a] fluoran, 3-diethylamino-benzo[c] fluoran, 3-dibutylamino-7-dibenzylaminofluoran , 3-dibutylamino-7-anilinofluoran , 3-diethylamino-7-anilinofluoran, 3-dibutylamino-6-methyl fluoran, 3-dibutylamino-6-methyl-7-anilinofluoran, 3-dibutylamino-6-methyl-7-(2,4-dimethylanilino) fluoran, 3-dibutylamino-6-methyl-7-(2-chloroanilino) fluoran, 3-dibutylamino-6-methyl-7-(4-chloroanilino) fluoran, 3-dibutylamino-6-methyl-7-(2-fluoroanilino) fluoran, 3-dibutylamino-6-methyl-7-(3-trifluoromethylanilino) fluoran, 3-dibutylamino-6-ethoxyethyl-7-anilinofluoran, 3-dibutylamino-6-chloro-anilinofluoran, 3-dibutylamino-6-methyl-7-(4-methylanilino) fluoran, 3-dibutylamino-7-(2-chloroanilino) fluoran, 3-dibutylamino-7-(2-fluoroanilino) fluoran, 3-dibutylamino-7-(N-methyl-N-formylamino) fluoran, 3-dipentylamino-6-methyl-7-anilinofluoran, 3-dipentylamino-6-methyl-7-(4-2-chloroanilino) fluoran, 3-dipentylamino-7-(3-trifluoromethylanilino) fluoran, 3-dipentylamino-6-chloro-7-anilinofluoran, 3-dipentylamino-7-(4-chloroanilino) fluoran, 3-pyrrolidino-6-methyl-7-anilinofluoran, 3-piperidino-6-methyl-7-anilinofluoran, 3-(N-methyl-N-propylamino)-6-methyl-7-anilinofluoran, 3-(N-methyl-N-cyclohexylamino)-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-cyclohexylamino)-6-methyl-7-anilinofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isoamylamino)-6-chloro-7-anilinofluoran, 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isobutylamino)-6-methyl-7-anilinofluoran, 3-(N-butyl-N-isoamylamino)-6-methyl-7-anilinofluoran, 3-(N-isopropyl-N-3-pentylamino)-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-ethoxypropylamino)-6-methyl-7-anilinofluoran, 3-cyclohexylamino-6-chlorofluoran, 2-methyl-6-p-(p-dimethylaminophenyl)aminoanilinofluoran, 2-methoxy-6-p-(p-dimethylaminophenyl)aminoanilinofluoran, 2-chloro-3-methyl-6-p-(p-phenylamino-phenyl)aminoanilinofluoran, 2-diethylamino-6-p-(p-dimethylaminophenyl)-amino-anilinofluoran, 2-phenyl-6-methyl--6-p-(p-phenylaminophenyl)aminoanilinofluoran, 2-benzyl-6-p-(p-phenylaminophenyl)aminoanilinofluoran, 3-methyl-6-p-(p-dimethyl-aminophenyl)aminoanilinofluoran, 3-diethylamino-6-p-(p-diethylaminophenyl)-aminoanilinofluoran, 3-diethylamino-6-p-(p-dibutylaminophenyl)aminoanilino-

fluoran, 2,4-dimethyl-6-[(4-dimethylamino)anilino] fluoran, 3-[(4-dimethylamino-phenyl)amino]-5,7-dimethylfluoran, 3,6,6'-tris(dimethylamino)spiro[fluorene-9,3'-phthalide], 3,6,6'-tris(diethylamino)spiro[fluorene-9,3'-phthalide], 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, 3,3-bis(p-dimethylamino-phenyl)phthalide, 3,3-bis-[2-(p-dimethylaminophenyl)-2-(p-methoxyphenyl)ethenyl-4,5,6,7-tetrabromophthalide, 3,3-bis-[2-(p-dimethylaminophenyl)-2-(p-methoxy-phenyl)ethenyl-4,5,6,7-tetrachlorophthalide, 3,3-bis[1,1-bis(4-pyrrolidinophenyl)-ethylene-2-yl]-4,5,6,7-tetrabromophthalide, 3,3-bis-[1-(4-methoxyphenyl)-1-(4-pyrridinophenyl)ethylene-2-yl]-4,5,6,7-tetrachlorophthalide, 3-(4-diethylamino-2-ethoxyphenyl)-3-(1-ethyl-2-methylindole-3-yl)-4-azaphthalide, 3-(4-diethylamino-2-ethoxyphenyl)-3-(1-octyl-2-methylindole-3-yl)-4-azaphthalide, 3-(4-cyclohexyl-ethylamino-2-methoxyphenyl)-3-(1-ethyl-2-methylindole-3-yl)-4-azaphthalide, 3,3-bis(1-ethyl-2-methylindole-3-yl) phthalide, 3,3-bis(1-octyl-2-methylindole-3-yl) phthalide, mixture of 2-phenyl-4-(4-diethylaminophenyl)-4-(4-methoxyphenyl)-6-methyl-7-dimethylamino-3,1-benzoxazine and 2-phenyl-4-(4-diethylaminophenyl)-4-(4-methoxyphenyl)-8-methyl-7-dimethylamino-3,1-benzoxazine, 4,4'-[1-methyl-ethylidene)bis(4,1-phenyleneoxy-4,2-quinazolinediyl)]bis[N,N-diethylbenzenamine], bis(N-methyldiphenylamine)-4-yl-(N-butylcarbazole)-3-yl-methane and mixtures thereof.

All of the above colour forming compounds can be used singly or as a mixture with other colour forming compounds, or they may also be used together with further black colour forming compounds.

Highly preferred are 3-diethylamino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-(3-methylanilino) fluoran, 3-diethylamino-6-methyl-7-(2,4-dimethylanilino) fluoran, 3-dibutylamino-6-methyl-7-anilinofluoran, 3-dipentylamino-6-methyl-7-anilinofluoran, 3-(N-methyl-N-propylamino)-6-methyl-7-anilinofluoran, 3-(N-methyl-N-cyclohexylamino)-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilinofluoran, 3-diethylamino-6-chloro-7-anilinofluoran, 3-dibutylamino-7-

(2-chloroanilino)fluoran, 3-N-ethyl-p-toluidino-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isobutylamino)-6-methyl-7-anilinofluoran, 3-N-ethyl-N-ethoxypropylamino-6-methyl-7-anilino-fluoran, 2,4-dimethyl-6-[(4-dimethylamino)anilino]fluoran, 3-(4-diethylamino-2-ethoxyphenyl)-3-(1-octyl-2-methylindole-3yl)-4-azaphthalide, 3,3-bis(p-dimethyl-aminophenyl)-6-dimethylaminophthalide and mixtures thereof.

It is also possible to use solid solutions comprising at least two colour forming compounds.

A monophase (or single-phase or guest-host) solid solution possesses a crystal lattice which is identical with the crystal lattice of one of its components. One component is embedded as the 'guest' in the crystal lattice of the other component, which acts as the 'host'. The X-ray diffraction pattern of such a monophase solid solution is substantially identical to that of one of the components, called the 'host'. Within certain limits, different proportions of the components produce almost identical results.

The term 'monophase solid solution' or 'multiphase solid solution' or mixed crystal', as defined herein, therefore, should be taken from the following definitions, which have been adapted to the current improved state of knowledge of such systems:
A monophase (or single-phase or guest-host) solid solution possesses a crystal lattice which is identical with the crystal lattice of one of its components. One component is embedded as the 'guest' in the crystal lattice of the other component, which acts as the 'host'. The X-ray diffraction pattern of such a monophase solid solution is substantially identical to that of one of the components, called the 'host'. Within certain limits, different proportions of the components produce almost identical results.

A multiphase solid solution possesses no precise, uniform crystal lattice. It differs from a physical mixture of its components in that the crystal lattice of at least one of its components is partially or completely altered. In comparison to a physical mixture of the components, which gives an X-ray diffraction diagram that is additive of the diagrams seen for the individual components. The signals in the X-ray diffraction diagram of a multiphase solid solution are broadened, shifted or altered in intensity. In general, different proportions of the components produce different results.

A mixed crystal (or solid compound type) solid solution possesses a precise composition and a uniform crystal lattice, which is different from the crystal lattices of all its components. If different proportions of the components lead, within certain limits, to the same result, then a solid solution is present in which the mixed crystal acts as a host.

For the avoidance of doubt it may also be pointed out that, *inter alia*, there may also be amorphous structures and mixed aggregates consisting of different particles of different physical type, such as, for example, an aggregate of different components each in pure crystal modification. Such amorphous structures and mixed aggregates cannot be equated with either solid solutions or mixed crystals, and possess different fundamental properties.

As hereinbefore detailed, the monophase solid solutions comprise a plurality of colour compounds. Suitable colour forming materials, which may be included in the solid solutions are those given above.

Of particular interest are the following monophase solid solutions: 3-dibutylamino-6-methyl-7-anilinofluoran and 3-dibutylamino-7-dibenzylamino-fluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-dibutylamino-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-diethylamino-7-anilinofluoran; 3-diethylamino-6-methyl-7-anilinofluoran and 3-diethylamino-7-

anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-diethylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-N-isoamyl-N-ethylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-N-2-pentyl-N-ethylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-N-isopropyl-N-ethylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-N-Cyclohexylmethyl-N-ethylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-dipropylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-N-2-butyl-N-ethylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-N-cyclohexyl-N-methylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-diethylamino-6-methyl-7-(3-methyl-anilino) fluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-diethylamino-6-methyl-7-(2,4-dimethylanilino) fluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-dipentylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-(N-methyl-N-propylamino)-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-diethylamino-6-chloro-7-anilino-fluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-dibutylamino-7-(2-chloroanilino)fluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-N-ethyl-p-toluidino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-(N-ethyl-N-isobutylamino)-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3-N-ethyl-N-ethoxypropylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 2,4-dimethyl-6-[(4-dimethylamino)anilino]fluoran; 3-N-isoamyl-N-ethylamino-6-methyl-7-anilinofluoran and 3-diethylamino-6-methyl-7-anilinofluoran; 3-diethylamino-6-methyl-7-anilinofluoran and 3-N-propyl-N-methylamino-6-methyl-7-anilinofluoran; 3-diethylamino-6-methyl-7-(3-tolyl)aminofluoran and 3-diethylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran and 3,3-bis(1-octyl-2-methylindol-3-yl)phthalide; 3-dibutylamino-6-methyl-7-anilinofluoran and mixture of 2-phenyl-4-(4-diethylaminophenyl)-4-(4-methoxyphenyl)-6-methyl-7-dimethyl-

amino-3,1-benzoxazine and 2-phenyl-4-(4-diethylaminophenyl)-4-(4-methoxy-phenyl)-8-methyl-7-dimethylamino-3,1-benzoxazine; 3-dibutylamino-6-methyl-7-anilinofluoran and 4,4'-[1-methylethylidene)bis(4,1-phenyleneoxy-4,2-quinazoline-diyl)]bis[N,N-diethylbenzenamine].

Usually in the above monophase solid solutions the first compound is in a molar ratio of 75 to 99.9% by mole, the second compound is in a ratio of 25 to 0.1% by mole.

Examples of monophase solid solutions comprising two components in the stated ratios are: 3-dibutylamino-6-methyl-7-anilinofluoran (99.9%), 3-diethylamino-6-methyl-7-anilinofluoran (0.1%); 3-dibutylamino-6-methyl-7-anilinofluoran (99%), 3-diethylamino-6-methyl-7-anilinofluoran (1%); 3-dibutylamino-6-methyl-7-anilino-fluoran (95%), 3-diethylamino-6-methyl-7-anilinofluoran (5%); 3-dibutyl-amino-6-methyl-7-anilinofluoran (90%) and 3-N-2-pentyl-N-ethylamino-6-methyl-7-anilino-fluoran (10%); 3-dibutylamino-6-methyl-7-anilinofluoran (95%) and 3-N-2-pentyl-N-ethylamino-6-methyl-7-anilinofluoran (5%); 3-dibutylamino-6-methyl-7-anilino-fluoran (90%) and 3-N-isopropyl-N-ethylamino-6-methyl-7-anilinofluoran (10%); 3-dibutylamino-6-methyl-7-anilinofluoran (95%) and 3-N-isopropyl-N-ethylamino-6-methyl-7-anilinofluoran (5%); 3-dibutylamino-6-methyl-7-anilinofluoran (90%) and 3-N-Cyclohexylmethyl-N-ethylamino-6-methyl-7-anilinofluoran (10%); 3-dibutyl-amino-6-methyl-7-anilinofluoran (95%) and 3-N-Cyclohexylmethyl-N-ethylamino-6-methyl-7-anilinofluoran (5%); 3-dibutylamino-6-methyl-7-anilinofluoran (90%) and 3-dipropylamino-6-methyl-7-anilinofluoran (10%); 3-dibutylamino-6-methyl-7-anilinofluoran (95%) and 3-dipropylamino-6-methyl-7-anilinofluoran (5%); 3-dibutylamino-6-methyl-7-anilinofluoran (90%) and 3-N-2-butyl-N-ethylamino-6-methyl-7-anilinofluoran (10%); 3-dibutylamino-6-methyl-7-anilinofluoran (95%) and 3-N-2-butyl-N-ethylamino-6-methyl-7-anilinofluoran (5%); 3-dibutylamino-6-methyl-7-anilinofluoran (90%), 3-diethylamino-6-methyl-7-anilinofluoran (10%); 3-dibutylamino-6-methyl-7-anilinofluoran (85%), 3-diethylamino-6-methyl-7-anilinofluoran (15%); 3-dibutylamino-6-methyl-7-anilinofluoran (80%), 3-

diethylamino-6-methyl-7-anilinofluoran (20%); 3-dibutylamino-6-methyl-7-anilinofluoran (95%), 3-N-isoamyl-N-ethylamino-6-methyl-7-anilinofluoran (5%); 3-dibutylamino-6-methyl-7-anilinofluoran (90%), 3-N-isoamyl-N-ethylamino-6-methyl-7-anilinofluoran (10%); 3-dibutylamino-6-methyl-7-anilinofluoran (80%), 3-N-isoamyl-N-ethylamino-6-methyl-7-anilinofluoran (20%); 3-dibutylamino-6-methyl-7-anilinofluoran (90%), 3-N-cyclohexyl-N-methylamino-6-methyl-7-anilinofluoran (10%); 3-diethylamino-6-methyl-7-anilinofluoran (90%), 3-N-isoamyl-N-ethylamino-6-methyl-7-anilinofluoran (10%); 3-diethylamino-6-methyl-7-anilinofluoran (80%), 3-N-isoamyl-N-ethylamino-6-methyl-7-anilinofluoran (20%); 3-diethylamino-6-methyl-7-anilinofluoran (20%), 3-N-isoamyl-N-ethylamino-6-methyl-7-anilinofluoran (80%); 3-diethylamino-6-methyl-7-anilinofluoran (10%), 3-N-isoamyl-N-ethylamino-6-methyl-7-anilinofluoran (90%); 3-diethylamino-6-methyl-7-anilinofluoran (90%), 3-N-propyl-N-methylamino-6-methyl-7-anilinofluoran (10%); 3-diethylamino-6-methyl-7-anilinofluoran (80%), 3-N-propyl-N-methylamino-6-methyl-7-anilinofluoran (20%); 3-diethylamino-6-methyl-7-anilinofluoran (20%), 3-N-propyl-N-methylamino-6-methyl-7-anilinofluoran (80%); 3-diethylamino-6-methyl-7-anilinofluoran (10%), 3-N-propyl-N-methylamino-6-methyl-7-anilinofluoran (90%); 3-diethylamino-6-methyl-7-anilinofluoran (10%), 3-diethylamino-6-methyl-7-(3-tolyl)aminofluoran (90%); 3-diethylamino-6-methyl-7-anilinofluoran (20%), 3-diethylamino-6-methyl-7-(3-tolyl)aminofluoran (80%); 3-dibutylamino-6-methyl-7-anilinofluoran (90%), 3,3-bis(1-octyl-2-methylindol-3-yl)phthalide (10%); 3-dibutylamino-6-methyl-7-anilinofluoran (80%), 3,3-bis(1-octyl-2-methylindol-3-yl)phthalide(20%); 3-dibutylamino-6-methyl-7-anilinofluoran (90%), mixture of 2-phenyl-4-(4-diethylaminophenyl)-4-(4-methoxyphenyl)-6-methyl-7-dimethylamino-3,1-benzoxazine and 2-phenyl-4-(4-diethylaminophenyl)-4-(4-methoxyphenyl)-8-methyl-7-dimethylamino-3,1-benzoxazine(10%); 3-dibutylamino-6-methyl-7-anilinofluoran (80%), mixture of 2-phenyl-4-(4-diethylaminophenyl)-4-(4-methoxyphenyl)-6-methyl-7-dimethylamino-3,1-benzoxazine and 2-phenyl-4-(4-diethylaminophenyl)-4-(4-methoxyphenyl)-8-methyl-7-dimethylamino-3,1-benzoxazine(20%); 3-dibutylamino-6-methyl-7-anilinofluoran (90%), 4,4'-[1-

methylethylidene)bis(4,1-phenyleneoxy-4,2-quinazolinediyl)]bis[N,N-diethylbenzenamine](10%); 3-dibutylamino-6-methyl-7-anilinofluoran (80%), 4,4'-[1-methylethylidene)bis(4,1-phenyleneoxy-4,2-quinazolinediyl)]bis[N,N-diethylbenzenamine] (20%).

The monophase solid solutions can be used singly or as a mixture with other colour forming compounds such as triphenylmethanes, lactones, fluorans, benzoxazines and spiropyrans; or they may also be used together with further black colour forming compounds. Examples of such other colour forming compounds are given hereinbefore.

The monophase solid solutions can be prepared by a variety of methods. One such method is the recrystallisation method wherein a physical mixture of the desired components is dissolved, with or without heating, in a suitable solvent or solvent mixture. Suitable solvents include but are not limited to toluene, benzene, xylene, dichlorobenzene, chlorobenzene, 1,2-dichloroethane, methanol, ethanol, iso-propanol, n-butanol, acetonitrile, dimethylformamide or mixtures of these solvents with each other and with water. The monophase solid solution is then isolated by crystallisation from the solvent or solvent mixture. This can be brought about by cooling, standing, addition of a further solvent to promote crystallisation or concentration by standard means such as distillation, steam distillation and vacuum distillation. When the monophase solid solution is isolated by concentration it may be advantageous to do so in the presence of a small amount of base, to improve the visual aspect of the isolated product.

Alternatively, monophase solid solutions can be prepared from mixtures of the appropriate starting materials. The technique can be used to produce mixtures of two or more fluorans or phthalides. For example, mixtures of two fluorans are produced by replacing a single starting material with two analogous materials to the same total molar concentration in the reaction. In the case of fluorans, these starting

materials are derivatives of amino phenols, phthalic anhydrides, keto acids and diphenylamines.

In addition, the heat sensitive recording material can contain additionally developers, unless the colour forming performance of the resultant heat sensitive material is disturbed thereby. Such developers are exemplified by but not limited to: 4,4'-isopropylidene bisphenol, 4,4'-sec-butylidene bisphenol, 4,4'-cyclohexylidene bisphenol, 2,2-bis-(4-hydroxyphenyl)-4-methylpentane, 2,2-dimethyl-3,3-di(4-hydroxyphenyl)butane, 2,2'-dihydroxydiphenyl, 1-phenyl-1,1-bis(4-hydroxyphenyl)butane, 4-phenyl-2,2-bis(4-hydroxyphenyl)butane, 1-phenyl-2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4'-hydroxy-3'-methylphenyl)-4-methylpentane, 2,2-bis(4'-hydroxy-3'-tert-butyllphenyl)-4-methylpentane, 4,4'-sec-butylidene-bis (2-methylphenol), 4,4'-isopropylidene-bis (2-tert-butylphenol), 2,2-bis(4'-hydroxy-3'-isopropylphenyl)-4-methylpentane, allyl-4,4-bis (4'-hydroxyphenyl) pentanoate, propargyl-4,4-bis(4'-hydroxyphenyl) pentanoate, n-propyl-4,4-bis (4'-hydroxyphenyl) pentanoate, 2,4-bis (phenylsulfonyl) phenol, 2-(4-methylsulfonyl)-4-(phenylsulfonyl) phenol, 2-(phenylsulfonyl)-4-(4-methylsulfonyl) phenol, 2,4-bis (4-methylphenylsulfonyl) phenol, pentamethylene-bis(4-hydroxybenzoate), 2,2-dimethyl-3,3-di(4-hydroxyphenyl)pentane, 2,2-di(4-hydroxyphenyl)hexane, 4,4'-dihydroxydiphenyl thioether, 1,7-di(4-hydroxyphenylthio)-3,5-dioxaheptane, 2,2'-bis(4-hydroxyphenylthio)diethyl ether, 4,4'-dihydroxy-3,3'-dimethylphenyl thioether; benzyl-4-hydroxybenzoate, ethyl-4-hydroxybenzoate, propyl-4-hydroxybenzoate, isopropyl-4-hydroxybenzoate, butyl-4-hydroxybenzoate, isobutyl-4-hydroxybenzoate, 4,4'-dihydroxydiphenyl sulfone, 2,4'-dihydroxydiphenyl sulfone, 4-hydroxy-4'-methyldiphenyl sulfone, 4-hydroxy-4'-isopropoxydiphenyl sulfone, 4-hydroxy-4'-butoxydiphenyl sulfone, 4,4'-dihydroxy-3,3'-diallyldiphenyl sulfone, 3,4-dihydroxy-4'-methyldiphenyl sulfone, 4,4'-dihydroxy-3,3',5,5'-tetrabromodiphenyl sulfone, 4,4'-bis (p-toluenesulphonylaminocarbonylamino) diphenylmethane, N-p-toluene-sulphonyl-N'-phenyl urea, dimethyl 4-hydroxyphthalate, dicyclohexyl 4-hydroxy-phthalate, diphenyl 4-hydroxyphthalate, 4-[2-(4-methoxyphenyloxy)ethyloxy]-

salicylate, 3,5-di-tert-butylsalicylic acid, 3-benzyl salicylic acid, 3-(α-methylbenzyl) salicylic acid, 3-phenyl-5-(α,α-dimethylbenzyl) salicylic acid, 3,5-di-α-methylbenzyl salicylic acid; metal salts of salicylic acid, 2-benzylsulfonylbenzoic acid, 3-cyclohexyl-4-hydroxybenzoic acid, zinc benzoate, zinc 4-nitrobenzoate, 4-(4'-phenoxybutoxy)-phthalic acid, 4-(2'-phenoxyethoxy)phthalic acid, 4-(3'-phenylpropyloxy)phthalic acid, mono (2-hydroxyethyl) -5-nitro-isophthalic acid, 5-benzyloxycarbonyl isophthalic acid, 5-(1'-phenylethanesulfonyl) isophthalic acid, bis(1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one-O)bis(thiocyanato-N) zinc and mixtures thereof.

The amounts of additionally developers can be chosen in the range of from 1 % by weight to 99 % by weight, based on the total amount of developers.

In addition, the heat sensitive recording material of the invention can contain a sensitiser. The weight ratio of sensitiser to colour former is usually chosen in the range of from 0.5:1 to 3:1, preferably 1:1 to 2:1, based on the total amount of the heat sensitive recording material.

Representative examples of sensitiser are stearamide, methylol stearamide, p-benzylbiphenyl, m-terphenyl, 2-benzyloxynaphthalene, 4-methoxybiphenyl, dibenzyl oxalate, di(4-methylbenzyl) oxalate, di(4-chlorobenzyl) oxalate, dimethyl phthalate, dibenzyl terephthalate, dibenzyl isophthalate, 1,2-diphenoxyethane, 1,2-bis(4-methylphenoxy) ethane, 1,2-bis(3-methylphenoxy) ethane, 4,4'-dimethylbiphenyl, phenyl-1-hydroxy-2-naphthoate, 4-methylphenyl biphenyl ether, 1,2-bis(3,4-dimethylphenyl) ethane, 2,3,5,6-4'-methyldiphenyl methane, 1,4-diethoxy-naphthalene, 1,4-diacetoxybenzene, 1,4-diproprionoxybenzene, o-xylylene-bis(phenyl ether), 4-(m-methylphenoxymethyl) biphenyl, p-hydroxyacetanilide, p-hydroxybutyranilide, p-hydroxynonananilide, p-hydroxylauranilide, p-hydroxy-octadecananilide, and N-phenyl-phenylsulphonamide.

The above sensitisers are known or can be prepared according to known methods.

In addition, the heat sensitive recording material of the invention can contain a stabiliser. The weight ratio of stabiliser : colour former is usually chosen in the range of from 0:1 to 2:1.

Therefore, a further preferred embodiment of the present invention relates to a heat sensitive recording material consisting essentially of

a) a substrate sheet, and

b) a heat sensitive colored image-forming layer formed on the surface of the substrate sheet and consisting essentially of

b1) a colour former compound

b2) the inventive mixture of colour developers,

b3) a stabilizer and/or a sensitizer.

Representative stabilisers for use in heat sensitive recording materials include 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-ethyl-6-tert-butylphenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-thio-bis(2-tert-butyl-5-methylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl) butane, 1,1,3-tris(2-methyl-4-hydroxy-5-cyclohexylphenyl) butane, bis (3-tert-butyl-4-hydroxy-6-methylphenyl) sulfone, bis (3,5-dibromo-4-hydroxyphenyl) sulfone, 4,4'-sulfinyl bis (2-tert-butyl-5-methylphenol), 2,2'-methylene bis (4,6-di-tert-butyl-phenyl) phosphate and alkali metal, ammonium and polyvalent metal salts thereof, 4-benzyloxy-4'-(2-methylglycidyloxy) diphenyl sulfone, 4,4'-diglycidyloxydiphenyl sulfone, 1,4-diglycidyloxybenzene, 4-[α-(hydroxymethyl)benzyloxy]-4-hydroxy-diphenyl sulfone, metal salts of p-nitrobenzoic acid, metal salts of phthalic acid mono benzyl ester, metal salts of cinnamic acid and mixtures thereof.

Preferred stabilisers are 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-thio-bis(2-tert-butyl-5-methylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl) butane, 1,1,3-tris(2-methyl-4-hydroxy-5-cyclohexylphenyl) butane, 4-benzyloxy-4'-(2-methylglycidyloxy) diphenyl sulfone and mixtures thereof.

Further preferred stabilizers are the following, which preferably can be used in amounts of less than 5 % by weight, based on the total weight of the heat sensitive recording material:
N-(p-toluenesulphonyl)-N'-phenylurea, N-(p-toluenesulphonyl)-N'-(o-tolyl)urea, N-(p-toluenesulphonyl)-N'-(m-tolyl)urea, N-(p-toluenesulphonyl)-N'-(p-tolyl)urea, N-(p-toluenesulphonyl)-N'-(p-n-butylphenyl)urea, N-(p-toluenesulphonyl)-N'-(o-chlorophenyl)urea, N-(p-toluenesulphonyl)-N'-(m-chlorophenyl)urea, N-(p-toluenesulphonyl)-N'-(2,4-dichlorophenyl)urea, N-(p-toluenesulphonyl)-N'-benzylurea, N-(p-toluenesulphonyl)-N'-(l-naphthyl)urea, N-(p-toluenesulphonyl)-N'-[1 -(2-methylnaphthyl)]urea, N-(p-toluenesulphonyl)-N'-(o-diphenyl)urea, N-(p-toluenesulphonyl)-N'-butylurea, N-(benzenesulphonyl)-N'-phenylurea, N-(p-chlorobenzenesulphonyl)-N'-phenylurea, N-(o-toluenesulphonyl)-N'-phenylurea, N-(p-toluenesulphonyl)-N'-methylurea, N-(p-toluenesulphonyl)-N'-ethylurea, N,N'-bis(p-toluenesulphonyl)urea, N-benzylsulphonyl-N'-phenylurea, N-(2-phenoxyethane)sulphonyl-N'-phenylurea, N-(4-methoxybenzyl)sulphonyl-N'-phenylurea, N-(2-(p-chlorophenyl)-ethane)sulphony]-N'-phenylurea, N-(p-biphenyl)sulphony]-N'-butylurea, N-benzylsulphonyl-N'-benzylurea, N-benzylsulphony]-N'-phenylthiourea, N-ethanesulphonyl-N'-1-naphthylurea, N-cyclohexanesulphonyl-N'-phenylurea, N-allylsulphonyl-N'-1-naphthylurea, N-(2-methoxy-ethanesulphonyl)-N'-biphenylurea, N-(2-tetrahydropyransulphonyl)-N'-1 naphthylurea, N-(2-allyloxyethanesulphonyl)-N'-1-naphthylurea, N-isopropane-sulphonyl-N'-benzylurea, N-isopropanesulphonyl-N'-(4-methylbenzyl)urea, N-methanesulphonyl-N'-(4-chloro-1-naphthyl)urea, N-isopropanesulphonyl-N'-(4-chloro-l-naphthyl)urea, N-methanesulphonyl-N'-1-naphthyl-thiourea, N-(p-toluene-sulphonyl)-N'-(p-methoxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(m-hydroxy-phenyl)urea, N-(p-toluenesulphonyl)-N'-(p-hydroxyphenyl)urea, N-(p-toluenesul-phonyl)-N'-(p-ethoxycarbonylphenyl)urea, N-(p-toluenesulphonyl)-N'-(2-phenoxy-ethyl)urea, N-benzylsulphonyl-N'-(2-phenoxyethyl)urea, N-benzylsulphonyl-N'-(p-methoxyphenyl)urea, N-(p-methoxybenzyl)sulphony]-N'-(2-(p-chlorophenyl-oxy)ethyl)urea, N-methanesulphonyl-N'-(2-phenoxyethyl)urea, N-methanesulphonyl-

N'-(4-methoxy-1-naphthyl)urea, N-(p-toluenesulphonyl)-N'-(3-n-butylaminosulphonylphenyl)urea, N-(p-toluenesulphonyl)-N'-(4-trimethylacetophenyl)urea, N-(benzenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(3-phenylsulphonyl-oxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(2-p-toluenesulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(2-phenyl- sulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(4-benzoyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(4-phenylsulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(4-acetoxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(2-p-toluenesulphonyloxy-5-ethylsulphonyl phenyl)urea, N-(o-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl)urea, N-(4-chlorobenzenesulphonyl)-N'-(3-p-toluene-sulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(4-p-toluenesulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(3-butylsulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(2-methyl-4-p-toluenesulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(5-p-toluene-sulphonyloxy-napthyl)urea, N-(p-toluenesulphonyl)-N'-(4-p-tolyloxysulphonylphenyl)urea, N-(p-toluenesulphonyl)-N'-(3-octylsulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(3-Hexadecylsulphonyloxyphenyl)urea, N-(octylsulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(4-phenylsulphonyloxyphenyl)urea, N-(phenylsulphonyl)-N'-(3-(p-toluenesulphonyloxy)phenyl)urea, N-(4-chlorophenylsulphonyl)-N'-(3-trimethylacetoxyphenyl)urea, N-(p-toluenesulphonyl)-N'-(4-(p-toluenesulphonyloxy)-phenyl)urea, N-(p-toluenesulphonyl)-N'-(4-acetophenyl)urea, N-(p-toluenesulphonyl)-N'-(4-acetamidosulphonylphenyl)urea, N-(p-toluenesulphonyl)-N'-(3-(ethoxycarbonyloxy)phenyl)-urea, N-(p-toluenesulphonyl)-N'-(3-(ethoxycarbamyl)phenyl)urea, N-(p-toluenesulphonyl)-N'-(3-(2-napthyl sulphonyloxy)phenyl)urea, N-(p-toluenesulphonyl)-N'-(4-benzoylphenyl)-urea, N-(p-toluenesulphonyl)-N'-(3-(4-toluenesulphonylamino)phenyl)urea, N-(p-toluenesulphonyl)-N'-(3-acetaminophenyl)urea, N-(4-chlorophenylsulphonyl)-N'-(4-trimethylacetamidophenyl)urea, N-(benzenesulphonyl)-N'-(4-trimethylacetamidophenyl)-urea, N-(4-chlorophenylsulphonyl)-N'-(2-(p-toluenesulphonyloxy)-phenyl)urea, N-(p-toluenesulphonyl)-N'-(3-(N,N-di-p-toluenesulphonyl)amino-

phenyl)urea, N-(benzene-sulphonyl)-N'-(2-(p-toluenesulphonyloxy)phenyl)urea, N-(4-chlorophenylsulphonyl)-N'-(4-acetamidosulphonylphenyl)urea, N-(p-toluene-sulphonyl)-N'-(3-(diphenylphosphinyl)phenyl)-urea;
bis(p-methoxybenzenesulphonylaminocarbonylamino)ketone, 1,2-bis(p-methoxy-benzene-sulphonylaminocarbonylamino)ethane, 1,5-bis(p-methoxybenzene-sulphonylamino-carbonylamino)-3-oxapentane, 1,3-bis(p-methoxybenzenesul-phonylaminocarbonylamino)-2-propane, 1,5-bis(p-methoxybenzenesulphonyl-aminocarbonylamino)-3-(2-(p-methoxy-benzenesulfonylaminocarbonylamino)ethyl)-3-azapentane, 1,3-bis(p-methoxybenzene-sulphonylaminocarbonylamino-methyl)benzene, 4,4'-bis(p-methoxybenzenesulphonylamino-carbonylamino) diphenylmethane, 4,4'-bis(p-methoxybenzenesulphonylaminothio-carbonylamino), diphenylmethane, 4,4'-bis(p-nitrobenzenesulphonylaminocarbonylamino)diphenyl-methane, 4,4'-bis(m-trifluoromethylmethoxybenzenesulphonylaminocarbonyl-amino)diphenylmethane, 4,4'-bis(p-phenoxybenzenesulphonylaminocarbonyl-amino)-diphenylmethane, 4,4'-bis(p-benzyloxybenzenesulphonyl aminocarbonyl-amino)diphenyl-methane, 4,4'-bis(p-acetylbenzenesulphonyl aminocarbonylamino)-diphenylmethane, 4,4'-bis(p-benzoylbenzenesulphonyl aminocarbonylamino)-diphenylmethane, 4,4'-bis(p-allyloxybenzenesulphonyl aminocarbonylamino)-diphenylmethane, 4,4'-bis(p-allyl-benzenesulphonyl aminocarbonylamino)-diphenylmethane, 4,4'-bis(p-ethyny-benzene-sulphonyl aminocarbonylamino)di-phenylmethane, 4,4'-bis(p-cyclohexylbenzene sulphonylaminocarbonylamino)-diphenylmethane, 4,4'-bis(p-phenylbenzenesulphonylamino-carbonylamino)di-phenylmethane, 4,4'-bis(p-benzylbenzenesulphonylaminocarbonylamino)-diphenylmethane, 4,4'-bis(o-methoxybenzenesulphonylaminocarbonylamino) diphenylmethane, 4,4'-bis(p-ethoxybenzenesulphonylaminothiocarbonylamino)-diphenylmethane, 2,2-bis(4'-(p-methoxybenzenesulphonylaminocarbonylamino)-phenyl)propane, 1,2-bis(4'-(p-ethoxybenzenesulphonylaminocarbonylamino)-phenyloxy)ethane, 3,3'-bis(p-methoxybenzenesulphonylaminocarbonylamino)-diphenylsulphone, 4,4'-bis(p-methoxybenzenesulphonylaminocarbonylamino)-diphenylether, 2,5-bis(p-methoxybenzenesulphonylaminocarbonylaminomethyl)-

furan, 1,3-bis(p-methoxybenzenesulphonylaminocarbonylamino)benzene, 1,5-bis(p-ethoxybonzene-toluenesulphonylaminocarbonylamino)naphthalene, bis(p-toluene-sulphonylamino-carbonyamino)ketone, 1,2-bis(p-toluenesulphonylaminocarbonyl-amino)ethane, 1,1,6,6-tetra(p-toluenesulphonylaminocarbonylamino)heptane, 1,5-bis(p-toluenesulphonyl-aminocarbonylamino)-3-oxapentane, 1,5-bis(p-toluene-sulphonylaminocarbonylamino)-3-thiopentane, 1,3-bis(p-toluenesulphonyl-aminocarbonylamino)-2-propanone, 1,5-bis(p-toluenesulphonylaminocarbony-lamino)3-[2'(p-toluenesulphonylaminocarbonyl-amino)ethyl]-3-azapentane, 1,3-bis(p-toluenesulphonylaminocarbonylamino)methylbenzene, 1,4-bis(p-toluene-sulphonylaminocarbonylamino)methylbenzene, 4,4'-bis(p-toluenesulphonylamino-carbonylamino)diphenylmethane, 4,4'-bis(o-toluenesulphonylaminocarbonylamino)}-diphenylmethane, 4,4'-bis(benzenesulphonylamniocarbonylamino)-diphenyl-methane, 4,4'-bis(l -naphthalenesulphonylaminocarbonylamino)-diphenylmethane, 2,2-bis[4'-(p-toluenesulphonylaminocarbonylamino)phenyl]propane, 1,2-bis[4'-(p-toluenesulphonyl-aminocarbonylamino)phenyloxy]ethane, 1,4-bis[3'-(p-toluene-sulphonylaminocarbonyl-amino)phenyloxy]ethane, 2,5-bis(p-toluenesulphonyl-aminocarbonylamino)methylfuran, 1,3-bis(p-toluenesulphonylaminocarbonyl-amino)benzene, 1,4-bis(p-toluenesulphonylamino-carbonylamino)benzene, 1,5-bis(p-toluenesulphonylaminocarbonylamino)naphthalene, 1,8-bis(p-toluene-sulphonylaminocarbonylamino)naphthalene, 4,4'-bis(p-toluenesulphonyl-amino-carbonylamino)diphenylether, 3,3'-bis(p-toluenesulphonylaminocarbonyl-amino)-diphenylsulphone, 4,4'-bis(p-toluenesulphonylaminocarbonyl-amino)diphenyl-sulphone, 2,4-bis(p-toluenesulphonylaminocarbonylamino)toluene, 2,6-bis(p-toluenesulphonylamino-carbonylamino)toluene, 4,4'-bis(p-toluenesulphonylamino-carbonylamino)diphenylsulphide, 3,4'-bis(p-toluenesulphonylaminocarbonyl-amino)diphenylether, 4,4-bis(methanesulphonyl-aminocarbonylamino)di-phenylmethane, 4,4'-bis(ethanesulphonylaminocarbonylamino)-diphenylmethane, 4,4'-bis(isopropanesulphonylaminocarbonylamino)diphenylmethane, 4,4'-bis(trifluoromethanesulphonylaminocarbonylamino)diphenylmethane, 4,4'-bis(cyclo-hexanesulphonylaminocarbonylamino)diphenylmethane, 4,4'-bis(allyl-

sulphonylamino-carbonylamino)diphenylmethane, 4,4'-bis(2-methoxyethane-sulphonylaminocarbonyl-amino)diphenylmethane, 4,4'-bis(2-tetrahydropyran-sulphonylaminocarbonylamino)-diphenylmethane, 4,4'-bis(2-allyloxyethane-sulphonylaminocarbonylamino)diphenylmethane, 1,5-bis(methanesulphonyl-aminocarbonylamino)naphthalene, 1,3-bis(methanesulphonyl-aminocarbonyl-amino)benzene, 4,4'-bis(methanesulphonylaminocarbonylamino)-diphenylether, 4,4'-bis(methanesulphonylaminothiocarbonylamino) diphenylmethane, 4,4'-bis(benzylsulphonylaminocarbonylamino)diphenylmethane, 4,4'-bis(p-methylbenzyl-sulphonylaminocarbonylamino)diphenylmethane, 4,4'-bis(p-methoxybenzylsulphonyl-aminocarbonylamino)diphenylmethane, 4,4'-bis(p-chlorobenzylsulphonylaminocarbonyl-amino)diphenylmethane, 4,4'-bis(2-phenoxyethylsulphonylaminocarbonylamino)-diphenylmethane, 4,4'-bis(2-(p-methoxyphenoxy)ethylsulphonylaminocarbonylamino) diphenylmethane, 4,4'-bis(benzylsulphonylaminocarbonylamino) diphenylether, 1,5-bis(benzylsulphonyl-aminocarbonylamino)naphthalene, 1,3-bis(benzylsulphonylamino-carbonylamino)-benzene, 4,4'-bis(benzylsulphonylaminothiocarbonylamino)-diphenylmethane, 1,3-bis(p-toluenesulphonylaminocarbonylamino)-2-methylbenzene, 1,4-bis(p-toluene-sulphonylaminocarbonylamino)-2,5-dimethylbenzene, 4,4'-bis(p-toluenesulphonyl-aminocarbonylamino)-3,3'-dimethyldiphenylmethane, 4,4'-bis(p-toluenesulphonyl-aminothiocarbonyl amino)-3,3'-dimethyldiphenylmethane, 4,4'-bis(o-toluenesul-phonylamino carbonylamino)-3,3'-dimethyldiphenylmethane, 4,4'-bis(benzene-sulphonyl aminocarbonylamino)-3,3'-dimethyldiphenylmethane, 4,4'-bis(p-toluene-sulphonylaminocarbonylamino)-3,3'-diethyldiphenylmethane, 4,4'-bis(p-toluene-sulphonyl-aminocarbonylamino)-3,3'-dichloro diphenylmethane, 4,4'-bis(p-toluene-sulphonyl-aminocarbonylamino)-3,3',5,5'-tetramethyldiphenylmethane, 4,4'-bis(p-toluenesulphonyl-aminocarbonyl amino)-3,3',5,5'-tetraethyldiphenyl-methane, 4,4'-bis(p-toluenesulphonyl aminocarbonylamino)-3,3'-dimethoxylbiphenyl, 4,4'-bis(p-to-luenesulphonylaminocarbonyl-amino)-3,3'-dimethylbiphenyl, 4,4'-bis(p-toluenesul-phonylaminocarbonylamino)-2,2',5,5'-tetrachlorobiphenyl, 2,8-dimethyl-3,7-bis(p-toluenesulphonylaminocarbonylamino)dibenzothiophene-5,5-dioxide, 4,4'-bis(p-

toluenesulphonylaminocarbonylamino)-3,3'-dimethyldiphenylether, 2,5-bis(p-toluenesulphonylaminocarbonylaminomethyl)-3,5-diethylfuran; N-(p-toluenesulphonyl)-N'-(pyrid-3-yl)urea, N-(p-toluenesulphonyl)-N'-(6-methylpyridin-2-yl)urea, N-(p-toluenesulphonyl)-N'-(5-methylisoxazol-3-yl)urea, N-(p-toluenesulphonyl)-N'-((1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazyol-3-one)4-yl)urea, N-(p-toluenesulphonyl)-N'-(1.H.-indazol-6-yl)urea, N-(p-toluenesulphonyl)-N'-(4,6-dimethylpyrimidin-2-yl)urea, N-(p-toluenesulphonyl)-N'-(benzothiazol-2-yl)urea, N-(p-toluenesulphonyl)-N'-(thiazol-2yl)urea, N-(p-toluenesulphonyl)-N'-(5-methyl-1.H.-pyrazol-3-yl)urea, N-(p-toluenesulphonyl)-N'-(benzimidazol-2-yl)urea, N-(p-toluenesulphonyl)-N'-(pyrimidin-2-yl)urea, N-(p-toluene-sulphonyl)-N'-(6-methanesulphonylbenzothiazol-2-yl)urea, N-(p-toluenesulphonyl)-N'-[4-(6-methyl-benzothiazol-2yl)phenyl]urea, N-(p-toluenesulphonyl)-N'-(1.H.-[1,2,4]triazol-3-yl)-urea.

All the exemplified stabilisers can be used singly or as a mixture with other stabilisers.

The heat sensitive recording material of the invention can be prepared according to conventional methods. For example, at least one colour forming compound, at least one developer and, if desired, at least one sensitiser are ground separately in water or a suitable dispersing medium, such as aqueous polyvinyl alcohol, to form an aqueous or other dispersion. If desired a stabiliser is treated in the same manner. The fine particle dispersions thus obtained generally are combined and then mixed with conventional amounts of binder, filler and lubricant. Usually the binder is used in a weight ratio in the range of from 0.5:1 to 4:1, preferably 3.5:1. The amount of filler and lubricant usually depends from the end application and as a rule is chosen by the manufacturer of the heat sensitive recording material in amounts well known to the person skilled in the art.

Representative binders used for the heat sensitive recording material include for example polyvinyl alcohol (fully and partially hydrolysed), carboxy, amide, sulfonic and butyral modified polyvinyl alcohols, derivatives of cellulose such as hydroxyethyl

cellulose, methyl cellulose, ethyl cellulose, carboxymethyl cellulose and acetyl cellulose, copolymer of styrene-maleic anhydride, copolymer of styrene-butadiene, polyvinyl chloride, polyvinyl acetate, polyacrylamide, polyamide resin and mixtures thereof.

Exemplary fillers, which can be used, include e.g. calcium carbonate, kaolin, calcined kaolin, aluminium hydroxide, talc, titanium dioxide, zinc oxide, silica, polystyrene resin, urea-formaldehyde resin, hollow plastic pigment and mixtures thereof.

Representative lubricants for use in heat sensitive recording materials include e.g. dispersions or emulsions of stearamide, methylene bisstearamide, polyethylene, carnauba wax, paraffin wax, zinc stearate or calcium stearate and mixtures thereof. Other additives can also be employed, if necessary. Such additives are for example fluorescent whitening agents and ultraviolet absorbers.

The coating composition so obtained can be applied to a suitable substrate such as paper, plastic sheet and resin coated paper, and used as the heat sensitive recording material. The system of the invention can be employed for other end use applications using colour forming materials, for example, a temperature indicating material, sterilisation indicating material.

The quantity of the coating is usually in the range of 2 to 10 g/m^2, most often in the range 4 to $8g/m^2$.

The recording material containing such a thermosensitive colouring layer can in addition contain a protective layer and, if desired, an undercoat layer. The undercoat layer may be interposed between the substrate and the thermosensitive colouring layer.

The protective layer usually comprises a water-soluble resin in order to protect the thermosensitive colouring layer. If desired, the protective layer may contain water-soluble resins in combination with water-insoluble resins.

As such resins conventional resins can be employed. Specific examples are: polyvinyl alcohol; starch and starch derivatives; cellulose derivatives such as methoxycellulose, hydroxyethylcellulose, carboxymethylcellulose, methylcellulose and ethylcellulose; sodium polyacrylate; polyvinyl pyrrolidone; polyacrylamide/acrylic acid ester copolymers; acrylamide/acrylic acid ester/methacrylic acid copolymers; alkali metal salts of styrene/maleic anhydride copolymers; alkali metal salts of isobutylene/maleic anhydride copolymers; polyacrylamide; sodium alginate; gelatin; casein; water-soluble polyesters and carboxyl-group-modified polyvinyl alcohols.

The protective layer may also contain a water-resisting agent such as a polyamide resin, melamine resin, formaldehyde, glyoxal or chromium alum.

Furthermore, the protective layer may contain fillers, such as finely-divided inorganic powders, e.g. of calcium carbonate, silica, zinc oxide, titanium oxide, aluminium hydroxide, zinc hydroxide, barium sulphate, clay, talc, surface-treated calcium or silica, or a finely-divided organic powder of, e.g., a urea-formaldehyde resin, a styrene/methacrylic acid copolymer or polystyrene.

The undercoat layer usually contains as its main components a binder resin and a filler.

Specific examples of binder resins for use in the undercoat layer are: polyvinyl alcohol; starch and starch derivatives; cellulose derivatives such as methoxycellulose, hydroxyethylcellulose, carboxymethylcellulose, methylcellulose and ethylcellulose; sodium polyacrylate; polyvinyl pyrrolidone; polyacrylamide/acrylic acid ester copolymers; acrylamide/acrylic acid ester/methacrylic acid copolymers;

alkali metal salts of styrene/maleic anhydride copolymers; alkali metal salts of isobutylene/maleic anhydride copolymers; polyacrylamide; sodium alginate; gelatin; casein; water-soluble polymers such as water-soluble polyesters and carboxyl-group-modified polyvinyl alcohols; polyvinyl acetate; polyurethanes; styrene/butadiene copolymers; polyacrylic acid; polyacrylic acid esters; vinyl chloride/vinyl acetate copolymers; polybutylmethacrylate; ethylen/vinylacetate copolymers and styrene/butadiene acrylic derivative copolymers.

Specific examples of fillers for use in the undercoat layer are:
finely-divided inorganic powders, e.g. of calcium carbonate, silica, zinc oxide, titanium oxide, aluminium hydroxide, zinc hydroxide, barium sulphate, clay, talc, surface-treated calcium, silica or calcined clay (e.g. Ansilex,Engelhard Corp.), and finely-divided organic powders of, e.g., urea-formaldehyde resins, styrene/methacrylic acid copolymers and polystyrene.

In addition, the undercoat layer may contain a water-resisting agent. Examples of such agents are given above.

In particular the invention provides exceptional resistance to plasticiser, oil and heat ageing whilst showing improved background whiteness, in particular after ageing at elevated temperature in a humid atmosphere.

Examples

Example 1: Preparation of heat sensitive coating formulations containing N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea and p-toluenesulphonylurea (99:1)

Dispersions A to C are prepared by grinding the compositions shown below in an attritor until an average particle size of 1 to 1.5 µm is attained.

Dispersion A (Colour Former)	
3-dibutylamino-6-methyl-7-anilinofluoran	3.01 parts
Polyvinyl alcohol (10% aqueous solution)	10.50 parts
Water	6.49 parts

Dispersion B (Colour Developer)	
N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea : p-toluenesulphonylurea. (99:1)	7.5 parts
Polyvinyl alcohol (10% aqueous solution)	7.5 parts
Water	22.5 parts

Dispersion C (Sensitiser)	
parabenzylbiphenyl	10.0 parts
Polyvinyl alcohol (10% aqueous solution)	10.0 parts
Water	20.0 parts

A thermal coating mixture is then prepared by combining together the following components:

	parts by weight
Dispersion A	6.6
Dispersion B	12.5
Dispersion C	6.0
Calcium Carbonate (25% aqueous dispersion)	13.2
Zinc stearate (33% aqueous dispersion)	1.5
Polyvinyl alcohol (10% aqueous solution)	6.5
Tinopal® ABP-X (fluorescent whitening agent)	0.12
Water	10.18

This coating mixture is applied on one side of a base paper weighing 50 g/m^2 in a coating weight of about 5.0 g/m^2 and then dried. The resulting sheet is calendered

by means of a laboratory calender to produce a recording sheet. The sheet so produced is subjected to a number of application tests, described below, the results are summarised in table 1.

Comparative Example 1: A heat sensitive recording paper is prepared as in Example 1 but using N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea as the sole developer in dispersion B.

The heat sensitive recording paper obtained demonstrates excellent background whiteness of paper after application of the coating liquid and in storage stability, i.e. resistance to ageing of the coated paper and excellent resistance of the image to cottonseed oil and plasticiser.

Examples 2-11: Heat sensitive recording papers are prepared according to example 1 but using the compositions shown below as the developer in dispersion B.

Ex.	Developer 1	wt-%	Developer 2	wt-%
2	N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea	99	p-toluenesulphonylurea	5
3	N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea	90	p-toluenesulphonylurea	10
4	N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea	85	p-toluenesulphonylurea	15
5	N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea	80	p-toluenesulphonylurea	20
6	N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea	75	p-toluenesulphonylurea	25
7	N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea	50	p-toluenesulphonylurea	50
8	N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea	85	napthylsulphonylurea	15
9	N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea	85	phenylsulphonylurea	15
10	N-(p-toluenesulphonyl)-N'-(3-p-toluenesulphonyloxyphenyl) urea	85	Hexadecyl sulphonylurea	15

DESCRIPTION OF TEST METHODS

Background Whiteness Before and After Ageing

This test assesses the effects of heat and moisture on unprinted thermal paper.

The whiteness of unprinted paper is measured using a Macbeth 1200 series Densitometer, before and after ageing for one hour at 60°C and 50% R.H.

Cottonseed Oil Resistance of Image

This test assesses the stability of the image when exposed to cottonseed oil.

An image is produced using an Atlantek thermal response tester model 200. Cottonseed oil is then Gravure printed onto the image which is then stored at 40°C for 24 hours. The optical density of the image is measured using a Macbeth 1200 series Densitometer before and after exposure.

Plasticiser Resistance of Image and Background

This test assesses the stability of the image and background when exposed to PVC containing 20 to 25% by weight of phthalate ester-type plasticiser.

An image is produced using an Atlantek thermal response tester model 200. The image is put into contact with the PVC under 107 g cm^{-2} pressure for 6 hours at 50°C, for examples 9-11 this test is extended to 24 hours. The optical density of the image and background are measured using a Macbeth 1200 series Densitometer before and after exposure.

Application Test Results

Ex.	Optical density of initial image	Background whiteness before aging	Background whiteness after ageing	Plastic - Image B/grd		Cottonseed oil resistance of image
Comp. Ex. 1	1.3	94	86	1.05[1]	90[2]	1.3
1	=	+	+	+	+	=
2	=	+	+	+	+	=

Ex.	Optical density of initial image	Background whiteness before aging	Background whiteness after ageing	Plastic - Image B/grd		Cottonseed oil resistance of image
3	=	+	+	+	+	=
4	=	+	+	+	+	=
5	=	+	+	+	+	=
6	=	+	+	+	+	=
7	=	+	+	+	+	=
8	-	+	+	=	+	-
9	=	+	=	+	=	=
10	=	+	=	+	=	=
11	=	+	-	+	=	=

Key = equal to comparative example 1

+ superior to comparative example 1

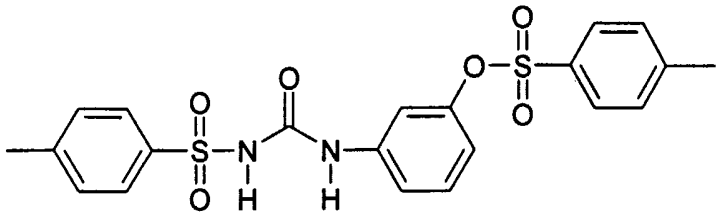
- inferior to comparative example 1

1 : 1.05 = Image density after test

2: 90 = background whiteness after test

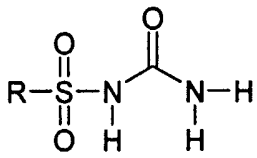
Claims

1. Mixture of colour developers comprising a compound of the formula I



I

and a compound of formula II



II

wherein

R^1 is C_1-C_{20}alkyl or C_6-C_{10}aryl, which can be substituted one to three times with halogen, C_1-C_4alkyl, -NR^2R^3, wherein R^2 and R^3 independently from each other stand for hydrogen or C_1-C_8alkyl, or C_1-C_8acyl amino.

2. Mixture according to claim 2, wherein the weight ratio of compound I to compound II is chosen in the range of from 999:1 to 1:1.

3. Heat sensitive recording material comprising

a) a substrate sheet, and

b) a heat sensitive colored image-forming layer formed on the surface of the substrate sheet and comprising

b1) a colour former compound

b2) the mixture of colour developers according to claim 1.

4. Heat sensitive recording material according to claim 3 consisting essentially of

a) a substrate sheet, and

b) a heat sensitive colored image-forming layer formed on the surface of the substrate sheet and consisting essentially of

b1) a colour former compound

b2) the mixture of colour developers according to claim 1,

b3) a stabilizer and/or a sensitizer.

5. Use of the mixture according to claim 1 for the manufacture of a heat-sensitive colored image-forming layer for the manufacture of heat-sensitive recording material.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/01897

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B41M5/30 B41M5/155

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 B41M

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00 35679 A (CIBA SC HOLDING AG ;HENSHALL JOHN BARRY (GB); TAYLOR JAMES PHILIP) 22 June 2000 (2000-06-22) page 1, paragraph 4 -page 4, paragraph 5 * Synthesis Example 4 * examples 1-11,25-27,29-37,49 & EP 1 140 515 A 10 October 2001 (2001-10-10) cited in the application	1,3,5

☐ Further documents are listed in the continuation of box C.

☒ 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 which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"T" later document published after the international filing date or priority date and not 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 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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 June 2003	01/07/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Markham, R

INTERNATIONAL SEARCH REPORT

International Application No
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