⑫ **EUROPEAN PATENT APPLICATION**

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�554 **Thermal imaging materials.**

㊷ Thermographic materials are colorless when unexposed, but provide an intense dark image when thermally addressed. The materials comprise white ferric organophosphate, ferric organophosphinate, or ferric organophosphonate in a clear binder with a colorless catechol or polycatechol held in said binder in solid solution. The choice of substituents on the catechol nucleus can give a change in the color of the thermal image together and provide good near infrared absorption. Use of mixed catechols can give achromatic black images. These combinations of materials show high stability at ambient temperatures.

EP 0 256 773 A2

THERMAL IMAGING MATERIALS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to thermographic materials. More particularly it relates to substantially colorless thermographic layers on a substrate. Many existing compositions exhibit a yellow or brown color cast which is caused by colored thermally sensitive metal compounds such as iron stearate. This invention uses compositions containing colorless iron salts which are thermally reactable to give a visible image.

In commercial applications, thermally developed labels are sought which not only provide visible images but which are also capable of being read by optical scanners using near infrared radiation (NIR). The images resulting from catechols with certain substituents exhibit low discrimination in the NIR. Other catechols give good discrimination both visually and to NIR.

2. Background of the Art

For many years heat-sensitive imaging sheets have been used for copying, thermal printing, thermal recording, and thermal labeling. Many of these materials involve thermally increasing the reactivity of two or more components of a color forming reaction which do not react at normal ambient temperatures. Reactivity is often enhanced by melting of one or both reactants which are physically separated from one another. Separation is accomplished either by dispersion in a single coated layer or by being situated in two different coated layers. Several general classes of color forming reactants have been used, of which two common ones are a) leuco lactone or spiropyran compounds reactable with phenolic compounds (e.g. U.S. 3,829,401 and U.S. 3,846,153) and b) heavy metal salts of organic acids

reactable with ligands to give colored complexes (e.g. U.S. 2,663,654, U.S. 3,094,620, U.S. 3,293,055 and U.S. 3,953,659).

Commercial preference for the heavy metal salt
5 class has often resulted from the high stability and near black color of the images produced (U.S. 4,531,141). Of the heavy metals used, iron, nickel, and cobalt are common and ferric iron appears to be preferred (U.S. 2,663,654, U.S. 3,953,659 and U.S. 4,531,141).
10 Two objections raised to the ferric salt – phenolic ligand systems are the colored nature of the unreacted ferric salt and the background stain often experienced because of the insidious, slow reaction of the two reactants on storage or during coating. Indeed, if the
15 reactants are intimately mixed they often react rapidly at room temperature (U.S. 3,442,682, U.S. 4,531,141). The first objection has led to the use of white fillers (U.S. 4,531,141) or other incident light scattering devices (e.g., "blushing" the surface of the layer as in U.S. 3,953,659) to
20 reduce the observed color tint of the coated layer. The second objection has led to the use of stabilizing compounds added to the reactive layer (U.S. 2,663,654, U.S. 3,442,682) and more particularly to the physical separation of the two reactants (U.S. 4,531,141) either by dispersion as separate
25 micro-particles (U.S. 2,663,654, U.S. 3,094,620, U.S. 3,111,423, and U.S. 3,293,055) or by separating the reactants in distinct but adjacent layers (U.S. 3,111,423 and U.S. 3,442,682).

As indicated earlier, a considerable list of heavy
30 metals has been used in their organic acid salt form to give thermographic images (U.S. 3,111,423 and U.S. 3,293,055). Some heavy metals giving colorless salts have been used and will be found amongst those listed in these two references. Such heavy metals (e.g., zinc), however, must be reacted
35 with ligands which themselves contribute color to the image and may indeed have a color cast before reaction. These

heavy metals have not successfully provided satisfactory
thermographic materials which are truly colorless and also
give a deep near black color on thermal exposure.

Thus the art discussed so far shows consistent
5 interest in two problems of ferric chelate imaging (a) the
colored nature of ferric organic acid salts and (b) the
difficulty in controlling the room temperature reactivity of
such salts with the range of ligands available.

More recently there has been interest evinced in
10 obtaining thermographically reactive iron salts which are
colorless and which give sharp, high density images when
reacted with a colorless ligand. Organo-phosphates of
ferric iron are known in the art to be amongst the few
colorless ferric salts (Smythe et al., J. Inorg. Nucl.
15 Chem., 30 1553-1561, (1968)). In U.S. 4,533,930 it is
disclosed that such organophosphates and the equivalent
thiophosphates can react with a variety of ligands under the
influence of heat to give colored results. Ferric salts of
organophosphinic acid and organophosphonic acids are
20 included. Some of these organophosphates and many of the
thiophosphates have some color cast before reaction which
appears to be obscured by the use of white filler in the
thermosensitive compositions. In the thermographic mate-
rials disclosed, the reaction of the ferric salt with the
25 ligand at ambient temperatures is precluded by either dis-
persing each reactant in microparticulate form in the binder
or by providing separate but adjacent layers for the two
reactants. These conditions are explicitly identified in
the claims by the wording "said metal compound and said
30 ligand compound being physically separated from one
another...". Also in this patent there are disclosed
pressure-sensitive manifold papers in which at least one of
the two reactants is encapsulated as a solvent solution.
When the microcapsules are burst by pressure, the reactants
35 come in contact and immediately react at room temperature to
give a colored result. This patent further discloses the

use of ferric organophosphates containing organic acid
moieties as formed by the aqueous reaction of a ferric salt,
an alkali metal organophosphate, and an alkali metal salt of
an organic acid. These are disclosed as giving the initial
5 material better "color forming properties" and giving better
image colors (Column 5 lines 38-39) than the simple organo-
phosphates. Excess organic acid salt is disclosed as
degrading the white color. It is of significance that the
inventors do not consider the choice of the ferric salt used
10 in the preparation to be important. In fact they specifi-
cally mention ferric chloride and ferric sulfate (Column 6
lines 10-17) and all of their examples use ferric chloride.

SUMMARY OF THE INVENTION

15   This invention provides thermographic layers which
are colorless when unexposed and are stable at room tempera-
tures but give intense dark colors when exposed to elevated
temperatures.

          These layers comprise a transparent binder, and at
20 least two thermal reactants which react with one another at
elevated temperatures; one of these reactants is in solid
solution in the binder, the other is dispersed in micro-
particulate form in the binder. Despite intimate contact
between the two reactants, no reaction occurs until the
25 temperature is elevated well above room temperature.

          The microparticulate reactant is chosen from a
class of ferric iron complexes in which the ligand is chosen
from organophosphates, organophosphinates, and organophos-
phonates which are colorless and which react with the second
30 reactant only at elevated temperature. The second reactant
is chosen from the class of catechols including polycate-
chols characterized by being colorless. Bis-catechols are
particularly preferred.

          The thermographic layers are coated or extruded
35 from coating mixes using non-aqueous solvents, which

solvents enable efficient milling of the ferric organophos-
phates, and provide a solution mixture of the binder and the
catechol.

A principal aspect of the invention is to provide
colorless thermographic sheets which give dark colored
images when addressed with elevated temperatures.

An aspect of the invention is to provide colorless
thermographic sheets which are stable at room temperatures.

A further aspect of the invention is to provide
colorless thermographic materials which are stable during
the process of coating and drying layers on a substrate.

Yet another aspect of the invention is to provide
colorless thermographic sheets which give thermal images
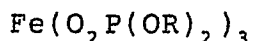exhibiting good discrimination when examined with near
infrared radiation (NIR).

Still another aspect of the invention is to pro-
vide colorless thermographic sheets which give black thermal
images exhibiting good visual discrimination and also good
NIR discrimination.

Iron(III) is the preferred metal for the thermal
reaction with catechol since it is capable of oxidizing the
catechol and generating iron complexes that are both black
in the visible and strongly absorbing in the near infrared.

Definitions: –

"polycatechol" molecules containing more than one
o-dihydroxybenzene moiety, the moieties being connected by
an organic connecting link which does not provide electronic
interaction between the moieties, such as a saturated
organic group (e.g., alkyl, cycloalkyl). This group
includes biscatechols.

"ferric organophosphate" compounds of the form
$$Fe(O_2P(OR)_2)_3$$
where R is an organic moiety such as alkyl, aryl, alphyl,
alicyclic groups, etc.

"ferric alkylphosphate" as above where R is an
alkyl moiety.

"chelate" in this case refers to the catechol and is normally bidentate but may be polydentate.
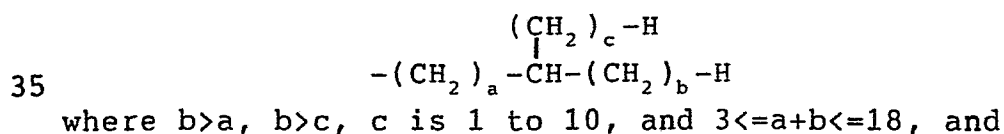
DETAILED DESCRIPTION OF THE INVENTION

U.S. 4,533,930 discloses a wide range of ferric salts of organo phosphorus oxyacids and thioacids as useful in thermographic reactions with a range of ligands. They are presented as giving much whiter backgrounds than ferric salts previously used in this art. It is clear from the examples and confirmed from our own investigations that the organothiophosphates are highly colored and dark. Furthermore, a great many of their examples using organophosphates record appreciable coloration of the compounds and whiteness levels are achieved by the use of fillers such as zinc oxide, aluminum hydroxide, and calcium carbonate.

This invention defines a preferred narrow range of ferric organophosphates which are entirely colorless, some of which are encompassed by the disclosure of U.S. 4,533,930 (I) whereas others are not (II). These compounds are di-alkylphosphates and have structures chosen from the general formulae

$$Fe[OOP(OR)_2]_3 \qquad\qquad (I)$$
$$and \quad Fe[OOP(OR)_2]_3 \cdot X \qquad (II)$$
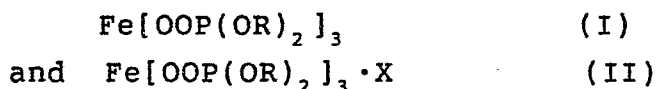
in which each R is selected independently from alkyl groups and substituted alkyl bearing substituents such as those selected from alkyl, cycloalkyl, and aryl providing that such substituents do not act as ligands or chelates for ferric ions.

Preferably R is selected from the group represented by the formula

$$-(CH_2)_a-\overset{\displaystyle (CH_2)_c-H}{\underset{\displaystyle |}{CH}}-(CH_2)_b-H$$

where $b>a$, $b>c$, c is 1 to 10, and $3<=a+b<=18$, and

X is selected from F^-, PF_6^-, Ph_4B^-, BF_4^-, NO_3^-, and $C_{14}H_{29}SO_4^-$

(where Ph = phenyl)

Our preferred compound is in formula I with a=1, b=4, and
5 c=2.

Previously used iron carboxylates typically are
too highly colored and cannot produce colorless backgrounds.
Dialkylphosphates are the preferred ligand for iron(III)
since the resulting complexes are completely colorless. .
10 Mixed dialkylphosphate/carboxylate iron complexes can be
made to be less colored than iron carboxylates, but they
still retain undesirable color because of the presence of
the carboxylate. The iron complexes of the sulfur analogues
of the carboxylates, phosphates, and their mixtures are
15 particularly undesirable since they are highly colored, even
black, materials.

If trialkylphosphates are used as the main ligand,
sufficiently stable iron complexes do not form, and if
monoalkylphosphates (as well as inorganic phosphates) are
20 used, generally undesirable, extensive crosslinking occurs
between metal centers such that the resulting iron
organophosphate is too stable to react with the catechol.
Aromatic phosphates often provide an iron complex that is
high melting, less reactive and more colored than the
25 dialkylphosphates.

The most preferred organophosphate ligands are
branched chain dialkylphosphates, and especially di-2-
ethylhexylphosphate (DEHP). Linear chain dialkylphosphates
form colorless iron complexes that give images with
30 catechols but are generally too unreactive (too highly
crosslinked) to provide sufficient image density. The
branch on the main chain should be sufficiently long and
sufficiently close to the metal center that crosslinking
between metal centers is inhibited. On the other hand, the
35 branch should not be too long or too close to the phosphorus
center since iron that is incompletely reacted with the

phosphate may result in a colored iron source, and would probably be too reactive in the coating solution. From a practical aspect, the ideal structure is illustrated by DEHP. The range for the side chain length might be best put 5 at about 1-10, the further from the connection point to the phosphorous the longer the chain. The length of the main chain is best illustrated by DEHP, that is, around 6-10. Chains as long as 18 are the practical maximum due to the required loading necessary to achieve suitable optical 10 density (i.e., molecular weight becomes impractically high). Asymmetric dialkylphosphates provide lower melting iron complexes.
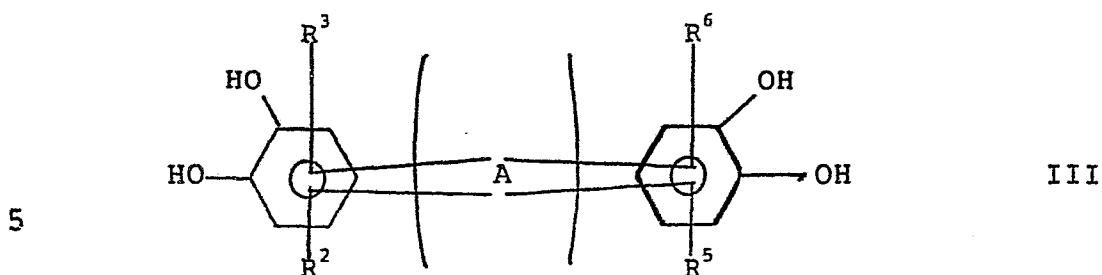
Alkyl phosphinic acids (in which the alkyl groups are attached directly to the phosphorus) show good thermal 15 reactivity with the catechols but are not preferred over the alkylphosphates. Apparently the higher pKa (insufficiently acidic) prevents them from forming a truly colorless, oligomeric complex. Ferric propyl(2-ethylhexyl)phosphinate, ferric cyclohexyl(2-ethylhexyl)phosphinate, and ferric 20 dicyclohexylphosphinate have been made and found to be . thermally reactive with catechols. Dialkyl-phosphonic acids (one R group attached directly to the phosphorus, the other attached via oxygen) have pKa's in between dialkylphosphates and dialkylphosphinic acids but have not been shown to be 25 useful. DEHP not only works well, it is commercially available in large quantities of relatively good purity.

Fe(DEHP)$_3$ is preferred in the iron organophosphate series. It is completely colorless, a major improvement over the iron carboxylates and mixed carboxylate/organo- 30 phosphate iron complexes. In addition, unlike the general straight chain dialkylphosphate iron complexes, it is very thermally reactive with the bis-catechols. It is also insoluble in the organic solvents required to coat this type of thermal imaging construction, unlike mixed 35 carboxylate/organophosphate iron complexes.

The chelate compounds which we select as thermal reactants with these iron compounds, are chosen to be color-less, to be non-reactive with the iron compounds at room temperatures even on intimate contact, to be rapidly

5 reactive at elevated temperatures above about 60°C, and to be easily soluble in organic solvents which are also solvents for the binder used. In this invention these chelates are preferably chosen from polycatechols and heavily ballasted monocatechols.

10   Common catechols are too reactive to be used with the preferred iron source in the preferred construction. Polyhydroxy catechols are similarly too reactive to be preferred.

        The preferred catechols are those in which two

15 catechol (specifically o-dihydroxybenzene) groups are part of the same molecule but in which the connecting group insures minimum electronic interaction between the catechol rings. They should not therefore be parts of the same aromatic ring system. The preferred connection between

20 catechols is alkylidene. Aromatic linkage would provide such electronic interaction between catechol groups that they would be too reactive. Aromatic linkages also give compounds which are colored and thus are precluded by the requirement that the chelate be colorless. Fused ring

25 connections, as illustrated by the preferred catechol, are excellent. Preparation of this compound, 1,1'-spirobi[-1H-indene]-5,5'-6,6-tetrol-2,2'3,3'-tetrahydro-3.3.3'3,'-tetramethyl, is known in the art. Heteroatomic fused ring connections are also acceptable. These are illustrated

30 in Formula III.

35

$$\text{HO} \quad \overset{R^3}{\underset{R^2}{\bigcirc}} \quad \overset{\displaystyle A}{} \quad \overset{R^6}{\underset{R^5}{\bigcirc}} \quad \overset{\text{OH}}{\underset{}{}} \quad \text{OH}$$

HO — OH   III

where A is a saturated ring system optionally containing
hetero atoms such as N, O, S, and

R^2, R^3, R^5 and R^6 are independently chosen from
forms which together alter the electronic character
(donating or accepting) of the OH groups on the ring. Such
groups include, but are not limited to H; halogen (F, Cl,
Br, and I); groups with no more than 10 atoms in the
backbone structure selected from C, N, S and O, (which may
of course be further substituted by additional groups such
as halogen); and aliphatic groups of up to 20 carbon atoms
(e.g., alkyl, ethers, thioethers, etc.) The heterogroups
with up to 10 carbon atoms includes heterocyclic and
aromatic groups as well as linear and branched groups.
Preferably these groups do not provide an acid hydrogen.
Preferably the groups are not chosen from substituents
comprising an acidic hydrogen linked to the aromatic ring
through a single atom chosen from O, S, and N, and

The two catechol units need not be symmetrical in
their substituents or their positioning.

The position of the o-hydroxy chelate site
relative to the connection site between the two catechol
groups is not critical. Substituents such as -OH, -SH, and
$-NH_2$ which contain acidic hydrogen can produce high
reactivity of the o-dihydroxy substituents and are therefore
not preferred in this invention.

Molecules containing more than two catechol groups
are also acceptable, as long as the connecting linkage
between the catechols meets the above requirements. Thus in

formulae IV, and V oligomers or polymers are illustrated
which are useful chelates in this invention

5

IV
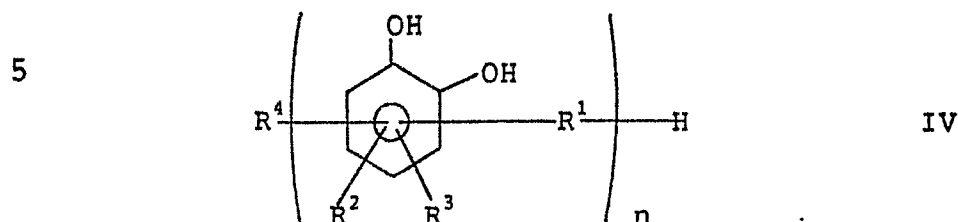
10

where R^2, R^3 are as defined above

R^4 is a capping substituent preferably -H or alkyl

R^1 is a bivalent linking group preferably

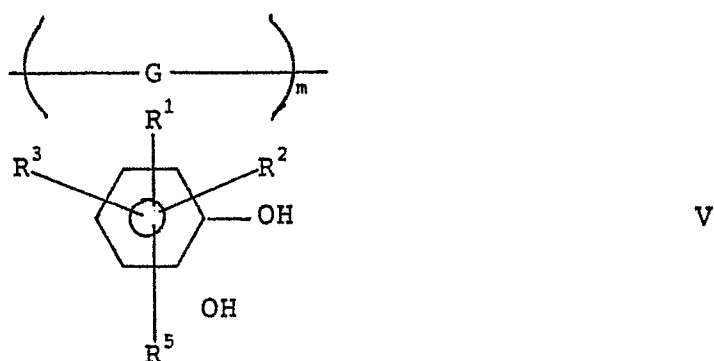alkylene, or a chain which may contain N, S, O, but may be

15 phenylene, naphthylene or combinations of these with the

proviso that R^1 does not facilitate electronic interaction

between the catechol moieties, and

n is an integer of 2 or more.

20

V

25

where R^2, R^3, and R^5 are defined above,

G is a unit in a polymer chain chosen from hydro-

30 carbons, alkyd, acryloid, polyester, phenol formaldehyde

resins etc. which are miscible with the binder used, and m

is an integer of 3 or more,

R^1 is either as defined above, or if G does not

facilitate electronic interaction between catechol moieties,

35 then R^1 need not be restricted in this way and in addition

to the definition above may be chosen from a single bond and
the groups defined for R^2, R^3 and R^5 above.

Monocatechols are in general too reactive for use
in this invention but if the ring is sufficiently ballasted
with a non-reactive ballasting group such catechols can be
used. Formula VI represents such ballasted monocatechols
useful in this invention.
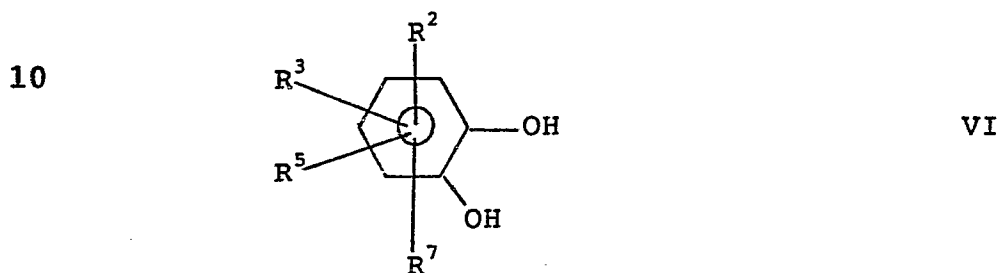
where R^2, R^3 and R^5 are defined above and R^7 is an alkyl
chain of eight or more carbon atoms.

The substituent groups R^2, R^3, R^4, R^5, and R^6 may
serve three functions: a) sterically constrain the molecule
to enhance or inhibit interactions between the reacted metal
centers, b) modify the solubility and melting point of the
catechol, and c) modify the electronic character of the
hydroxy groups by withdrawing or donating electron density
to the chelating site.

One of the most important functions of the R group
is the control of the electronic properties of the catechol,
in order to control the color of the final image. Commonly
known electron donating R groups (such as alkyl, mono- or
di-alkyl substituted amino, alkoxy, etc.) enable the
catechol to be oxidized more readily by the iron, which is
important for obtaining the infrared absorption properties
(at 905 nm in particular) needed for bar code readers. A
green complex results upon imaging this material with iron.
Conversely, commonly known electron withdrawing R groups
(such as nitro, ammonium, halogen, etc.) inhibit oxidation
of the catechol by the iron. The resulting complex will

tend to remain a violet-blue. The combination of catechols
containing both electron donating and electron withdrawing
groups provides for an imaging construction that is able to
generate both a desirable black visible image and a high
5 contrast image in the near infrared. The connecting linkage
between the catechol groups may be used to control all three
functions, a) - c), if the R groups are built into the
connecting linkage.

The proper choice of the substituents on each
10 catechol in the bis-catechol or polycatechol molecule can
give the desired mixture of visible and NIR absorption
properties. Alternatively the physical mixture of catechols
with the different substituents can give similar results.

A number of bis-catechols are available commer-
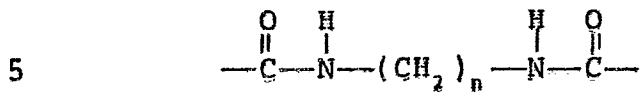15 cially e.g., nordihydroguaiaretic acid.

20
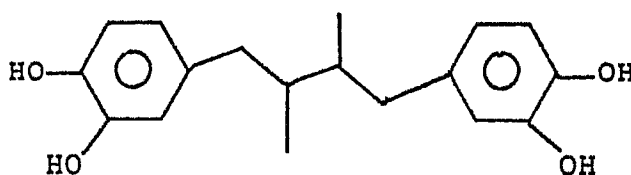
Preparation of polycatechols is disclosed in
Rodgers et al. J. A. C. S., 107, 4094 (1985) and in Anderson
& Hiller, "Development of Iron Chelators for Clinical Use"
25 DHEW Publ. No. (NIH) 76-994 p. 137. These polycatechols may
be represented by the formula:

30
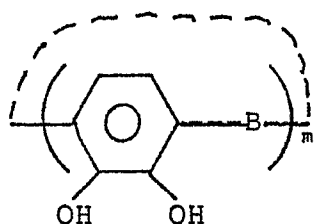
wherein B comprises the atoms in an organic
35 bridging group necessary to complete a cyclic structure with
the included catechol moiety or moieties and m is 1 to 10,

preferably 1 to 4. B is preferably comprised of C and N
ring atoms and is more preferably selected from

5

$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_n-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-$$

wherein n is 1 to 20, preferably 1 to 4. Rodgers et al.,
supra, shows the formation of monomers, dimers, trimers,
tetramers, pentamers, and hexamers having these
10 diaminoalkine linkages.

Of particular importance to this invention is that
the chelate and the binder are soluble in a common solvent
and that after coating and drying off the solvent the
chelate remains in solid solution in the binder. The ferric
15 alkylphosphates are not soluble either in the solvent or in
the binder and are thus dispersed in the latter as micro-
particles which are in intimate contact with the chelate in
solid solution. These two reactants exhibit very poor reac-
tivity even at elevated temperatures if they are physically
20 separated in the binder by using dispersed microparticles of
the chelate as well as the ferric alkylphosphate. In the
practice of this invention these classes of chelate exhibit
very low reactivity at room temperature but good reactivity
at elevated temperatures.

25 Binders suitable in this invention are poly-
acrylate and methacrylate and their copolymers vinyl resins,
styrene resins, cellulose resins, polyester resins,
urethanes, alkyl resins, silicones, and epoxy resins.
Generally the resins must be miscible with non-aqueous
30 solvents and have a melting point above the reaction temper-
ature of the ferric compound and chelate. The binder should
also be transparent.

A coating composition suitable to make a thermal
recording sheet can be made in the following manner. The
35 ferric alkylphosphate (I or II) is dispersed in a solvent
such as acetone, methyl ethyl ketone, ethanol, etc., by ball

milling. To this dispersion a polymer binder and a chelate
(III, IV V or VI) both soluble in the chosen solvent are
added and agitated until dissolved. The coating composition
may then be coated on a suitable substrate and dried at
5 temperatures below thermal reaction temperatures.

Substrates which may be used are films of trans-
parent, opalescent, or opaque polymers, paper, optionally
with white or colored surface coatings, glass, ceramic, etc.
The substrate must be stable and undistorted at the thermal
10 reaction temperatures which are preferably between 60° and
200°C and more preferably between 80° and 150°C.

We have found that the preparation of the color-
less ferric organophosphate compounds I is not as simple as
U.S. 4,533,930 suggests. Their method involves mixing
15 aqueous solutions of an alkali metal salt of the organophos-
phoric acid and a ferric salt of a strong mineral acid such
as hydrochloric and sulfuric, which results in a precipitate
of the ferric organophosphate. It has been found that
ferric chloride which is preferred by the patent gives
20 slightly colored precipitate even with alkyl phosphates
whereas those from ferric nitrate are completely colorless.
The preferred preparation therefore uses ferric nitrate to
give compounds I and II.

Ferric alkylphosphate compounds II where
25   X = fluoride, hexafluorophosphate, tetraphenyl-
borate, tetrafluoroborate, tetradecylsulfate, and
nitrate.

This may be prepared by mixing required equivalent
quantities in aqueous solution of ferric nitrate, alkali
30 metal salt of the alkylphosphoric acid, and the alkali metal
salt of the acid HX. Compound II then precipitates.

When X = acetate, however, the acetate ion is too
soluble in water to remain attached to the ferric alkylphos-
phate and the result is the compound I again. If the
35 ferric nitrate and alkali metal alkylphosphate are
dissolved in glacial acetic acid, then compound II for X =

nitrate is precipitated. This compound and the fluoride may
also be prepared using ethyl alcohol as solvent and adding
potassium acetate or sodium fluoride to the ferric nitrate
and alkali metal phosphate in required equivalent amounts.

5   It is of interest to note that the disclosure of
U.S. 4,533,930 says that any carboxylic or thiocarboxylic
acid may be used to form "composite iron salt" by reacting
ferric chloride, an organic phosphoric acid and the
carboxylic acid in an aqueous medium. The patent says that
10 non-white salts are precipitated if the carboxylic acid is
in excess. Their preferred carboxylic acids contain 5 or
more carbon atoms. Our experimental evidence is that the
composite iron salts obtained by their methods are of the
form (leaving thio equivalents aside)

15

$$Fe(OOPR'_2)_y(OOCR)_x$$
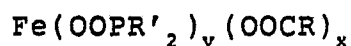
· where y + x = 3 and R, R' can be a wide range of aliphatic
and aromatic substituents. R = CH_3 cannot be obtained by
20 their preparation as we have disclosed above.

          The following are preparative examples for the
ferric alkylphosphates I and II.

Example A

25 Preparation of $Fe(DEHP)_3$

          1. The method is similar to (but using ferric
nitrate instead of ferric sulfate) the literature
preparation of L. E. Smythe, T. L. Whateley and R. L. Werner
(J. Inorg. Nucl. Chem., 30, 1553 (1968)). To 2.0 g KOH in
30 175.0 ml H_2O is added 10.0 g DEHP. This solution is added
over 5 minutes to 35.0 ml of water containing 4.0 g
$Fe(NO_3)_3 \cdot 9H_2O$ with vigorous stirring. The mixture is
stirred 10 minutes, filtered, washed in fresh water with
stirring, filtered and dried under vacuum at 70°C to a
35 constant weight. An-off white solid is obtained . The
infrared spectrum shows the expected phosphate stretches, as

well as small amounts of OH, and the characteristic ethyl
group presence at 1466.1 cm^{-1}. The Differential Scanning
Calorimeter (DSC) revealed a melting point endotherm of this
complex at 120°C.

5   2. To 1.0 liters of water is added 16.8 g KOH.
To a separate 1.5 liters of water is dissolved 11.0 g NaBF$_4$,
then 38.2 g Fe(NO$_3$)$_3$·9H$_2$O. While the iron salt is
dissolving, 97.7 g DEHP is added to the rapidly stirred KOH
solution. The thick phosphate solution is added rapidly to
10 the iron solution with mechanical stirring. The pure white,
rubbery solid is filtered, washed with stirring, filtered
and dried. It is important that the source of iron(III) is
not ferric chloride as it gives a yellow product. DSC shows
a melting point endotherm of the material at 145°C. The
15 infrared spectrum of a vacuum dried (room temperature)
sample reveals the expected phosphate stretches, but unlike
1 (above) there is no presence of OH.

     3. Example A1 may also be carried out at elevated
temperatures (60°C) with no disadvantageous effects. The
20 same endotherm behaviour in the DSC is obtained as in A1.

Example B
Preparation of Fe(DEHP)$_3$(nitrate)

     Powdered Fe(NO$_3$)$_3$·9H$_2$O, 80.8 g, is dissolved in
25 800 ml glacial acetic acid. As soon as a clear solution is
obtained, 193.0 g bis-(2-ethylhexyl)phosphate (DEHP) is
added in a rapid dropwise manner with vigorous stirring.
Less than a stoichiometric amount of DEHP gives a more
colored product; an excess of DEHP is not disadvantageous.
30 The white product is filtered, washed with acetic acid and
dried under vacuum. The approximate yield is 84%. The
product is found to be rubbery and may be recrystallized by
precipitation from cyclohexane by acetone. If FeCl$_3$ is used
in place of the nitrate, a clear yellow acetic acid solution
35 results.

Alternative preparation from ethanol: To 40 ml of absolute ethanol is added 2.0 g $Fe(NO_3)_3 \cdot 9H_2O$. Upon dissolution, 5.0 g DEHP are added, and the clear solution stirred 5 minutes. An aqueous solution of potassium acetate

5　(0.5 g in 4.5 g H_2O) is added dropwise. The mixture is stirred 2 minutes, filtered, redispersed in water, stirred an additional 20 minutes, filtered and vacuum dried. The infrared spectrum is identical to that prepared from acetic acid.

10　　　　Characterization: The infrared spectrum clearly shows the coordinated organophosphate (1000-1200 cm-1) and nitrate (1551.0 cm-1 asymmetric stretch, the symmetric stretch is under other peaks), and the absence of Fe-O-Fe stretches. DSC shows a small exotherm centered around 215°C

15　followed by the main endotherm centered at 282°C. The complex is readily soluble in cyclohexane, and is an excellent film forming material when coated on a substrate (clear, colorless film). Elemental analysis is consistent with the presence of one nitrate, and confirms the 3:1 P:Fe

20　ratio. Magnetic susceptibility determined by the Evan's NMR method (J. Chem. Soc., 2003 (1959), demonstrates a high spin iron complex. The complex was also found to be conductive in cyclohexane solution.

25　Example C

Preparation of $Fe(DEHP)_3F$

　　　1. To 500.0 g H_2O is added 6.0 g KOH. To a separate 500.0 g H_2O is added 12.0 g $Fe(NO_3)_3 \cdot 9H_2O$ followed by 0.62 g NaF. To the aqueous base solution is added 32.0 g

30　DEHP, which is then added rapidly to the mechanically stirred iron solution. The pure white iron complex is filtered, washed and vacuum dried.

　　　2. To 300 ml ethanol is added 16.13 g $Fe(NO_3)_3 \cdot 9H_2O$. Upon dissolution, 40.0 g DEHP is added

35　rapidly dropwise (3 minutes). The clear solution is stirred 5 minutes then 3.2 g NaF in 32 g H_2O are added dropwise (5

minutes). The white solid is stirred, then diluted with 400
ml H_2O, stirred 30 minutes and filtered. A colorless solid
results. Elemental analysis is consistent with a 3:1:1
P:Fe:F ratio.

5

Example D
Preparation of $Fe(DEHP)_3$ (tetradecylsulfate)
        A mixture of 1.06 g tetradecylsulfate in 100 g H_2O
with 1.2 g $Fe(NO_3)_3 \cdot 9H_2O$ yields an orange precipitate which
10 is immediately treated with 3.2 g DEHP and 0.6 g KOH in 50
ml H_2O. After stirring 3 days a white solid is filtered and
air dried. The infrared spectrum is consistent with the
proposed material.

15 Example E
Preparation of $Fe(DEHP)_3$ (tetraphenylborate)
        To 1.1 g sodium tetraphenylborate and 1.0 g
$Fe(NO_3)_3 \cdot 9H_2O$ in 40 ml H_2O is added rapidly 3.2 g DEHP and
0.73 g KOH in 80 ml H_2O. The mixture is filtered, dispersed
20 in water, stirred, filtered and air dried. The infrared
spectrum is consistent with the proposed material.

Example F
Preparation of $Fe(DEHP)_3(Fe(CN)_6)$
25   This example illustrates that the choice of the
counter ion is important in determining the color of the
complex. Because it is colored, this complex is not
preferred in this invention.
        To 25.0 g H_2O is added 0.61 g KOH, 3.2 g DEHP and
30 then 1.2 g $K_4(Fe(CN)_6) \cdot 3H_2O$. A total of 1.2 g $Fe(NO_3)_3 \cdot 9H_2O$
are added, and the mixture shaken over 6 days. A brown
solid results which is filtered and dried. It exhibits an
infrared spectrum that shows the presence of the phosphate
and the $Fe(CN)_6$ groups.

35

The following are examples of the preparation of
ferric organophosphinates useful in this invention.

Example G

5 Preparation of ferric n-propyl(2-ethylhexyl)phosphinate
        To a solution of 25 g of n-propyldichlorophos-
phineoxide in 300 ml of petroleum ether, 28 g of
diethylamine in 150 ml of petroleum ether was added over 4
hours. The petroleum ether was removed by distillation and
10 the remaining n-propyl (diethylamine)chlorophosphine oxide
was distilled off under vacuum.
        The Grignard of 1-bromo-2-ethylhexane (31 g) was
prepared in ether, and 26.4 g of the n-propyl(diethylamine)-
chlorophosphine oxide was added to it at room temperature
15 and refluxed for 72 hours. The resulting solution was
treated with 5M hydrochloric acid and refluxed overnight.
On cooling the n-propyl (2-ethylhexyl)phosphinic acid was
extracted with petroleum ether and distilled to give a
colorless liquid (B.P. = 172-180°C at 0.12 mm Hg).
20   To 1.3 g of $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in 5 g of
glacial acetic acid, 2.7 g of the prepared organophosphinic
acid was added. This solution was diluted with 9 parts of
water rapidly. The ferric n-propyl(2-ethylhexyl)phosphinate
appeared as a white solid precipitate which was filtered
25 off, washed with water, and dried in air.

Example H

Preparation of ferric dicyclohexylphosphinate
        The dicyclohexylphosphinic acid was made by the
30 method disclosed in Smythe et al., supra. A solution of 1.3
g of $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in 50 ml water was prepared.
In a solution of 0.66 g of KOH in 10 g of water, 2.35 g of
the phosphinic acid was dissolved. This was diluted with 50
ml water and added rapidly to the solution of ferric
35 nitrate. A fine yellow precipitate occured which was

filtered off, washed with water, and air dried to give the
ferric dicyclohexylphosphinate.

Example I
5 Preparation of ferric cyclohexyl(2-ethylhexyl)phosphinate
          Using the method described in Example G, 30 g of
cyclohexyldichlorophosphine oxide was used in place of the
n-propyl dichlorophosphine oxide to give a thick colorless
oil. The white ferric cyclohexyl(2-ethylhexyl)phosphinate
10 was obtained by the treatment described in Example H.

          The following are examples of thermographic
materials according to this invention.

15 Definition of Terms used in Examples
          Bkgd - total optical reflectance density of the
unimaged sheet using a MacBeth RD504 or MacBeth TR924
densitometers.
          I.D. - Maximum optical reflection density of the
20 image areas.
          - This is color of the background. Measured with
Hunter Labscan II using 2 degree Observer for Illuminant C
and specified in "L-a-b" units.
          L,a,b - the luminance and the two color
25 coordinates for the measured surface color using the "L-a-b"
color solid.
          PCR - Print contrast ratio at wavelength of 900 nm
where

30
$$PCR = \frac{R(Bkgd) - R(I.D.)}{R(Bkgd)}$$

and R are the reflectance values equivalent to the indicated
measured densities measured with MacBeth PCM-II
35 Print/contrast meter or RJS Enterprises Codascan 3600.

Initiation Temperature is temperature at which an optical density of 0.05 above the background is reached.

Example 1 - Green Image

5   A dispersion of the iron tris(di-2-ethylhexyl)-phosphate (I) was formed by ball milling for 24 hours 25 grams of (I) in 75g of acetone using flint glass marbles. To 4.0 g of this dispersion was added 3.27 g of 15% ethylacrylate methyl methacrylate copolymer resin in acetone 10 and 0.5 g of the 1,1'-spirobi[-1H-indene]-5,5'-6,6-tetrol-2,2'3,3'-tetrahydro-3.3.3'3,'-tetramethyl(II). This was agitated till (II) dissolved. This was coated on 2 mil opaque titanium dioxide filled polyester at 2.5 mil oriface using a knife coater and allowed to air dry. The resulting 15 thermal recording sheet exhibited excellent whiteness giving a blue image which changed to green within four hours.

Bkgd = 0.09 I.D. = 0.84 initiation temperature = 129°C Initial PCR = 0.45; PCR after 12 hours = 0.76; Color with Hunter 2C, L = 92.37, a = -2.07, b = 3.56.

20

Example 2 - Purple Image

Same as Example 1 using tannic acid (MCB reagent) in place of (II). This gave a thermal recording sheet with a white background and a purple image which was stable and 25 did not change color.

Bkgd = 0.12; I.D.= 1.09; Initiation temp. = 120°C; PCR = 0.19 measured 12 hours after imaging. Color with Hunter 2 C, L = 89.84, a = -1.19, b = 5.06.

30 Example 3 - Black Image

A thermal recording sheet was prepared as in Example 1 substituting 0.4 g of (II) and 0.1 g of tannic acid for (II). The thermal recording sheet exhibited a white background with a bluish-purple image which turned 35 black within 4 hours.

Bkdg = 0.11; I.D.= 1.13; Initiation temp = 122°C;

PCR = 0.45 increasing to 0.58 within 12 hours. Color with
Hunter 2 C, L = 91.09, a =-1.60, b = 3.56.

Example 4 - Peroxide Green Image

5   A thermographic recording sheet was prepared
following Example 1 but with the addition of 0.08 g of
t-buty(peroxy-benzoate (Aldrich Chem) and immediately
coated. The resulting sheet had a light green background
with an immediate vibrant green image upon imaging.

10   Bkgd = 0.12; I.D. = 1.02; PCR = 0.87; Color with
Hunter 2 C, L = 83.97, a = -7.08, b = 8.50.

Example 5 - Peroxide Black Image

        Same as Example 3 but with 0.08 g of t-butyl-
15 peroxybenzoate and coating immediately. The resulting
thermal recording sheet had a very light green background
which gave an immediate black image color.

        Bkgd = 0.12; I.D. = 1.24; PCR = 0.73; Color with
Hunter 2C, L = 84.43, a = -5.05, b = 5.74.

20

Example 6 - Phenidone

        A thermal recording sheet was prepared as in
Example 1 with the addition of .5 g of a 5% solution in
acetone of phenidone A (1-phenyl-3-pyrazolidinone, 95%
25 Aldrich) onto the formulation. This gave excellent pot life
eliminating any premature reaction and also gave improved
sheet stability. This noticeably whiter thermal recording
sheet had the following properties.

        Bkgd = 0.11; I.D. = 0.71; Initiation temp. =
30 131°C; Initial PCR = 0.50 increasing to 0.70 within 12
hours. Color Hunter 2 C; L = 92.79, a = -1.48, b = 3.83;
Side by side control with this example showed Bkgd = 0.12;
ID = 0.84.

35

Example 7 - Paper

        Same as Example 5 but coated on a 46 1b paper (24
x 36 x 500 basis) giving a sheet with good whiteness.

        Bkdg = 0.09; ID = 0.72; Initiation temperature =
5 125.2°C, Color with Hunter 2C, L = 91.03, a = -1.28, b
= -5.31.

Example 8 - Nitrate

        A dispersion of 25 g iron tris(di-2-ethylhexyl)
10 phosphate nitrate was made with 48.75 g Acetone and 1.25 g
cellulose acetate by ball milling with flint glass balls for
24 hours. A coating dispersion was prepared from 6.0 g of
this dispersion, 5 g of a 12% solution of cellulose acetate
in acetone, and 9.0 g of a 10% solution of 1,1',spirobi[-H-
15 indene]-5,5',6,6'-tetol-2,2',3,3'-tetrahydro-3,3,3',3'tetram
ethyl(II) in acetone coated at 2 mils wet thickness on 46#
(24" x 36" x 500) paper, and air dried. This thermal
recording sheet gave a blue image changing to green within 4
hours.
20   Bkg = 0.16, ID = 0.52, initiation temp. of 152°C.

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30

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WHAT IS CLAIMED IS:

1. A colorless thermographic material comprising
a transparent film-forming binder, an organic solvent
soluble colorless catechol in solid solution in said binder,
and colorless or substantially colorless microparticles of a
ferric iron compound selected from ferric organophosphates,
ferric organophosphinates, and ferric organophosphonates
dispersed in said binder.

2. A colorless thermographic material as recited
in claim 1 wherein said colorless catechol is selected from
(a)
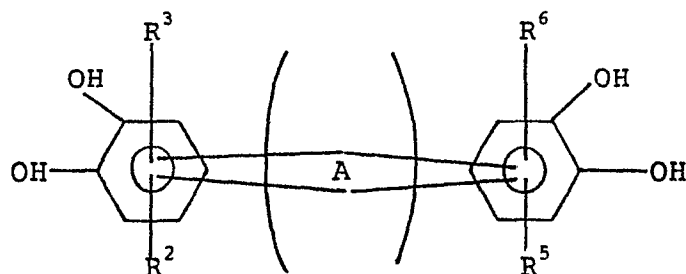
where A is a saturated ring system optionally
containing hetero atoms selected from N, O, and S,
R^2, R^3, R^5, R^6 are independently chosen from H,
and electron donating, and electron withdrawing groups
consisting of H and no more than 5 atoms chosen from C, N,
O, and S,
(b)
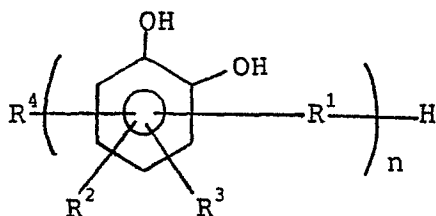
where R^2, R^3 are defined above,
R^4 is a capping group chosen from H and alkyl (C_1
$-C_8$),

R^1 is a bivalent linking group having saturated bonds at either end selected from alkylene, a chain containing at least one of N, S, O, phenylene, and naphthylene having no more than 12 carbon and hetero atoms, said linking

5 group R^1 being chosen such that it does not facilitate electronic interaction between the catechol moieties nor produce with the two catechol hydroxy groups a polydentate chelate,

(c)

10

15
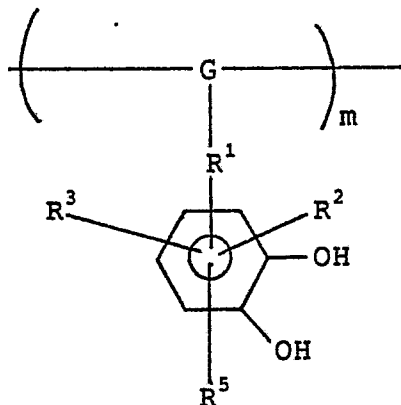
where R^2, R^3 and R^5 are defined above

20 G is a unit from a polymer chain chosen from hydrocarbons, alkyd, acryloid, polyester, and phenol formaldehyde resins which are miscible with said binder,

R^1 is as defined above or if G does not facilitate electronic interaction between catechol moieties, then R^1

25 need not be restricted in this way and in addition to the definition above may be chosen from a single bond and the groups defined for R^2, R^3 and R^5 above,

and m is an integer greater than 2; and

(d)

30

35
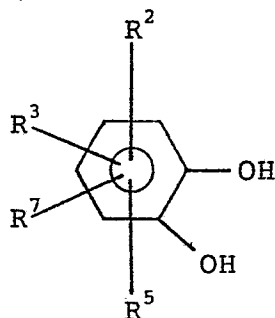
where R^2, R^3, R^5, are defined above and R^7 is an alkyl chain
of eight or more carbon atoms

3. A colorless thermographic material according
to claim 1 wherein said ferric iron compound is selected
from

a) $Fe[OOP(OR)_2]_3$
b) $Fe[OOP(OR)_2]_3 \cdot X$
c) $Fe[OOPR(OR)]_3$, and
d) $Fe[OOPR_2]_3$

where each R is independently selected from alkyl groups
substituted with substituents selected from alkyl,
cycloalkyl, and aryl groups, providing that said
substituents do not act as ligands or chelates for ferric
ions, and X is selected from fluoride, hexafluorophosphate,
tetraphenylborate, tetrafluoroborate, tetradecylsulfate, and
nitrate.

4. A colorless thermographic material according
to claim 1 wherein said ferric organophosphate is selected
from

(a) $Fe[OOP(OR)_2]_3$ and
(b) $Fe\{OOP(OR)_2]_3 \cdot X$

where each R is selected independently from the group
represented by the formula

$$-(CH_2)_a-\overset{\displaystyle (CH_2)_c-H}{\underset{\displaystyle |}{CH}}-(CH_2)_b-H$$

where $1 \le c \le 10$
      $b > a$, $b > c$, and
      $3 \le a + b \le 18$

10. A sheet material according to claim 9 in which B has the formula

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_n-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-$$

wherein n is an integer from 1 to 4 and m is an integer of from 1 to 4.