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(54) **PEINTURE A L'HUILE**
(54) **OIL-BASED PAINT**

(57) An oil-based artist paint composition is disclosed in which a plasticizer is included that acts to circumvent embrittlement of a dried paint film on ageing. The invention has particular application to artists' paint compositions that are linseed oil based. A preferred plasticizer is butyl polyacrylate. In a preferred embodiment, alkyd resins are included in the composition to reduce the tendency of paint films to shrink on ageing and "creep" when used in very heavy impasto applications.

ABSTRACT

IMPROVED OIL-BASED PAINT

An oil-based artist paint composition is disclosed in which a plasticizer is included that acts to circumvent embrittlement of a dried paint film on ageing. The invention has particular application to artists' paint compositions that are linseed oil based. A preferred plasticizer is butyl polyacrylate.

In a preferred embodiment, alkyd resins are included in the composition to reduce the tendency of paint films to shrink on ageing and "creep" when used in very heavy impasto applications.

- 1 -

IMPROVED OIL-BASED PAINTFIELD OF THE INVENTION

This invention relates to artist paints and more particularly to an improved linseed oil-based artist paint and a medium therefor.

BACKGROUND TO THE INVENTION

Traditional artist paints are oil-based wherein the oil is generally linseed oil. Such paints have been in use for at least the past three centuries and continue to retain popularity. Oil-based paints are often used in conjunction with a medium which allows the artist to adjust the rheology of the paint and adjust the pigment/binder ratio.

It has long been recognised that whilst linseed oil-based artist paints have many desirable properties, in use they suffer from two defects.

The first defect is a tendency to yellow. This has been found to be controllable within acceptable limits by a careful formulation.

The second and most serious defect is that of an uncontrollable tendency to become brittle with age. It is understood that this embrittlement is caused by continued polymerisation of the linseed oil, a process which cannot be arrested at any desired stage of "cure". This defect is particularly acute in both large and thickly painted oil paintings.

In order to circumvent these defects, the prior art has provided acrylic artist paints. It is notable that acrylic paints have achieved considerable popularity and that these paints do not suffer from the two defects of linseed oil-based artist paints. However, acrylic paint does not possess the "feel" of traditional oil-based artist paints. For that reason these paints are not generally used by "serious" artists.

Other attempts at meeting the embrittlement defect

- 2 -

have been based on discovering formulations that were used by the various "old masters". None of these attempts, to the present inventor's knowledge, have proved satisfactory.

Two other problems encountered in the use of artists' oil paints are shrinkage and "creep". Ageing oil paint films shrink as they age, and at a time in their ageing cycle when they are already too brittle to accommodate such movement without cracking.

"Creep" results, for example, in very heavy impasto applications of paint which often shrink and move about while the underlayers are still wet, causing the surface to crinkle

SUMMARY OF THE INVENTION

The present inventor has recognised that there exists a need for a linseed oil or other oil based artist paint that will not only have the right "feel" but will not embrittle on aging, or suffer from shrinkage or where applicable, "creep".

To meet the need to reduce embrittlement, the inventor proposes the introduction of an agent or agents into the paint that will act to plasticise the oil.

It follows that mediums for use with such a paint are also required and hence such mediums will also incorporate the requisite oil plasticiser.

Accordingly, a first aspect of the present invention consists in an improvement to an oil-based artist paint composition wherein the improvement comprises including in the composition an effective amount of a plasticiser for the oil, wherein the ratio of the plasticiser to the oil is no more than 20% plasticiser to 80% oil.

In a second aspect, the present invention further consists in an improvement to a medium composition for use with an oil-based artist paint wherein the improvement comprises including in the medium composition an effective amount of a plasticiser for the oil.

- 3 -

It will be recognized by those skilled in the art that the mediums of the invention may also be used with a traditional linseed oil-based artist paint, to impart the beneficial properties of the invention thereto.

5 Although the present invention is useful for a variety of oil-based paints, it is preferred that the oil is selected from sunflower, safflower and linseed oils. Particularly preferred is linseed oil where the colour of the paint composition will not be adversely affected by
10 the yellowing or darkening of the linseed oil with time. In those paint compositions that are light in colour, sunflower oil or safflower oil are preferred.

The present inventor believes that a selection of plasticiser and inclusion at an appropriate level in the
15 paint and/or medium will produce paintings, the paint film of which when aged will contain sufficient soft polymer to ensure that film integrity and a degree of pliability are maintained.

Many soft polymers are potentially satisfactory for
20 use in the inventive compositions however, in selecting suitable polymers, it will be recognised that the polymer must have the following properties:

- 1) A great degree of flexibility which remains unaltered by aging indoors. It is noted that the greater the
25 flexibility, the smaller the addition required.
- 2) Non-yellowing.
- 3) Compatible with raw linseed oil and solvents that are mixed with linseed oil.
- 4) Unaffected by any of the constituents of the linseed
30 oil per se (acid free).

DESCRIPTION OF THE INVENTION

In the paint composition of the present invention, two polymers that have been found to perform satisfactorily as plasticisers are butyl polyacrylate and
35 polyvinyl chloride isobutylether resin. These are

- 4 -

available from BASF under the trade names Acronal™ 4F and Laroflex™ MP25, respectively. Acronal™ 4F is most preferred since the Laroflex is somewhat viscous. Additionally, it is a soft resin (copolymer) rather than a plasticiser per se so that substantial amounts are need to achieve the effect of the Acronal.

Other polymeric plasticisers that are operable are, for example, epoxidized oils such as Paraplex™ G62, available from Rohm & Haas.

10 The common monomeric plasticisers are not recommended as over a time frame of say ten years, volatilisation would lead to their loss, thereby resulting in embrittlement and shrinkage of the oil paint film.

15 It would appear that a ratio of up to 20% polymer to 80% oil, particularly linseed oil, is possible without noticeably altering the "feel" of the paint. It is to be expected that the desired improvement in film characteristics should be achieved with polymer ratios of 7-20%.

20 To meet the shrinkage and "creep" problems a non-yellowing thermoplastic resin may be included in the inventive paint composition, preferably with at least one alkyd resin. Desirably, the at least one alkyd resin will be thixotropic and will act to aid in the through drying of the oil and maintain "balance" in handling properties. 25 A second alkyd resin may be advantageously included to aid in the through drying of the oil.

One non-yellowing thermoplastic resin that has been found suitable is Laropal™ A81, which is available from BASF. Two alkyd resins that have been found suitable are 30 Jordathix™ and Jordasol™, both of which are available from Ashland Chemicals. These are long oil alkyd resins.

Without wishing to be bound by theory, the present inventor believes that the presence of an alkyd resin 35 triggers the drying process with the oils used. By

- 5 -

selection and combination of two alkyd resins and by appropriately formulating the other components of a paint composition of the invention, the characteristics of the paint will be such that its handling properties will
 5 appear entirely conventional. Additionally, the slower drying sunflower or safflower oils can be made to dry at much the same speed as linseed oil.

In order to more fully appreciate the nature of the invention, several examples of typical paint compositions
 10 of the invention are set out below.

The examples show the formulation of a number of different pigment types:

- titanium white
- burnt umber
- 15 - red oxide
- pthalo blue

Burnt umber is an inherently thixotropic pigment with a high oil demand.

Red oxide is a characteristically strong inorganic
 20 pigment requiring an intermediate level of extender.

Pthalo blue is an organic pigment with a requirement for a high level of extender.

In addition, two extenders are exemplified, kaolin with a high oil demand and calcite with a low oil demand.

25 EXAMPLE 1

Titanium White

	<u>Ingredient</u>	<u>Parts by weight</u>
	Pigment	300
	Laropal (50%)	200
30	Jordathix (40%)	130
	Jordasol (70%)	100
	Sunflower oil	150
	Swelling clay	80
	Calcite	450
35	Acronal 4F	80

- 6 -

EXAMPLE 2Red Oxide

	<u>Ingredient</u>	<u>Parts by weight</u>
	Pigment	200
5	Laropal (50%)	270
	Linseed oil	220
	Jordathix (40%)	120
	Jordasol (70%)	50
	Acronal 4F	80
10	Kaolin	250
	Swelling clay	100

EXAMPLE 3Burnt Umber

	<u>Ingredient</u>	<u>Parts by weight</u>
15	Pigment	375
	Laropal (50%)	250
	Jordathix (40%)	120
	Jordasol (70%)	50
	Acronal 4F	80
20	Linseed oil	250
	Swelling clay	70
	Calcite	250

EXAMPLE 4Beta Pthalo Blue

	<u>Ingredient</u>	<u>Parts by weight</u>
25	Pigment	60
	Laropal (50%)	281
	Jordathix (40%)	100
	Jordasol (70%)	50
30	Linseed oil	200
	Swelling clay	85
	Acronal 4F	80
	Kaolin clay	300

To each of these compositions may be added other
 35 ingredients well known in the art such as dispersants and

- 7 -

viscosity modifiers. Further ingredients well known in the art such as drying agents, will be included in the paint compositions at a level appropriate to the compositions.

5 To prepare Examples 1-3, the swelling clay is dispersed in the Laropal, Jordathix and Jordasol. The requisite pigment and oil is then added followed by the Acronal 4F and the calcite or kaoline. Drying agents and other minor ingredients are then mixed into the
10 composition as appropriate.

 To prepare Example 4, a premix of the pigment is made with the Laropal. The premix is added to the remaining ingredients after they have been suitably mixed. Drying agents and other minor ingredients may be mixed into the
15 composition as appropriate.

 It should be noted that the ratio of the liquid components of these examples may be considerably varied. For example, to achieve a satisfactory rheology, the thixotropic Jordathix and low viscosity Laropal solutions,
20 at high concentration, are "balanced out". The Acronal and Jordasol which both have high viscosity need to be compensated for by the Laropal and Jordathix.

 In the medium composition of the present invention, polymers that have been found to be satisfactory are
25 polyvinyl chloride isobutyl ether copolymer (Laroflex MP25), butyl polyacrylate (Acronal 4F) and epoxidised oil (available from Rohm and Haas under the trade name Paraplex G62).

 It is noted that prior art mediums are commonly oleo
30 resinous blends in a solvent, having 20-40% solids, according to the artist's preference. The proportion of oil to resin determines the oiliness of the "feel", the higher the proportion of oil, the oiler, less tacky is the "feel".

35 In a medium composition of the present invention the

- 8 -

plasticising polymer may be used in place of part or all of the resinous component in an oleo resinous blend. It is noted that Laroflex MP25 may be used without an oil component.

5 By way of example, a typical medium composition comprises polyvinyl chloride isobutyl ether copolymer in a solvent, having approximately 30% solids. The formulation is prepared by methods well known in the art.

The medium composition of the present invention is
10 suitable for use with oil-based paints.

Alkyd resins are used where paint is to be applied thickly. Without the addition of alkyd resins, where paint is applied thickly the paint film will dry on the surface while remaining soft underneath. Movement of the
15 soft underlayer may cause wrinkling of the surface. Inclusion of an alkyd resin allows the paint to set after application.

In order to better understand the nature of the medium composition of the invention, set out below are
20 three examples.

EXAMPLE 1 "FAT GEL"

	<u>Ingredient</u>	<u>Parts by weight</u>	<u>Resin Solids</u>
	Jordasol	400	280
	Jordathix	200	80
25	Turpentine	100	
	Acronal 4F (10% solids)	36	

This is a syrupy medium for glazing at 51% solids.

EXAMPLE 2 "HEAVY GEL"

	<u>Ingredient</u>	<u>Parts by weight</u>	<u>Resin Solids</u>
30	Jordasol	600	420
	Jordathix	200	80
	Laropal (50%)	400	200
	Swelling clay	160	
	Acronal 4F	80	80
35	and drying agents		

- 9 -

This composition has a paste consistency suitable for impasto techniques and a solids content of 60.9%.

EXAMPLE 3 "LEAN LIQUID GEL"

	<u>Ingredient</u>	<u>Parts by weight</u>
5	Jordathix	300
	Jordasol	300
	Turpentine	450
	Acronal 4F 10%	33
	and drying agents	

10 This is a main medium used to dilute paint and has a solids content of 33%.

Although the invention has been described with reference to certain preferred embodiments and examples, the person skilled in the art will appreciate that
15 numerous variations and modifications may be made to the invention without departing from the spirit or scope thereof as broadly described.

**THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:**

1. An improved oil-based artist paint composition exhibiting reduced embrittlement on aging, said composition comprising:
 - an oil selected from the group consisting of linseed oil, rape seed oil, soya, cottonseed, sunflower oil and safflower oil,
 - a pigment,
 - an extender, and
 - a polymeric plasticizer compound selected from the group consisting of an acrylate polymer or copolymer, a soft resin copolymer, an epoxidized oil and a polyester, said polymeric plasticizer compound being present in an amount effective to plasticize said composition such that the weight ratio of said polymeric plasticizer compound to oil varies according to the oil absorbency of said pigment and is in the range of from 7:93 to 33.3:100.
2. A paint composition as in claim 1, wherein the plasticizer is an epoxidized oil or a polyester.
3. A paint composition as in claim 1 including a non-yellowing thermoplastic resin in an amount effective to reduce both creep of heavy impasto applications and shrinkage of aged films of said composition.

4. A paint composition as in claim 1 including at least one alkyd resin which is thixotropic and is present in an amount effective to aid through drying of the oil.
5. A paint composition as in claim 4 in which the composition contains two alkyd resins, one of which is thixotropic and both are present in amounts effective to aid through drying of the oil.
6. A paint composition as in claim 5 wherein the thixotropic alkyd resin is present in an amount of from 40-52 parts by weight and the other alkyd resin is present in an amount of from 35-70 parts by weight.
7. A paint composition as in claim 3 wherein the non-yellowing thermoplastic resin is present in an amount of from 100 to 140.5 parts by weight.
8. A paint composition as in claim 7 wherein the oil is linseed oil.
9. A paint composition as in claim 8 wherein the plasticiser is an epoxidized oil.
10. A paint composition as in claim 9 wherein the epoxidized oil is present in an amount of 80 parts by weight.

11. A medium composition for use with an oil-based artist paint comprising:

a solvent;

at least one alkyd resin which is thixotropic and is present in an amount effective to aid through drying of oil in an oil-based artist paint; and

a polymeric plasticizer compound selected from the group consisting of an acrylate polymer or copolymer, a soft resin copolymer, an epoxidized oil and a polyester, effective to plasticize an oil-based artist paint and in an amount such that when the medium composition is used with an oil-based artist paint, the weight ratio of said polymeric plasticizer compound to oil will be in the ratio of 7:93 to 33.3:100;

said medium composition having a resin solids content of from 33 to 60.9%

12. A medium composition as in claim 11 wherein the plasticiser is an epoxidized oil or a polyester.

13. A medium composition as in claim 12 including two alkyd resins, one of which is thixotropic and both are in amounts effective to aid through drying of the oil in said paint.

14. A medium composition as in claim 13 including a non-yellowing thermoplastic resin in an amount effective to reduce both creep of heavy impasto applications and shrinkage of aged films of said paint.

15. A medium composition as in claim 14 wherein the thixotropic alkyd resin is present in an amount of from 80-120 parts by weight and the other alkyd resin is in an amount of from 210-420 parts by weight.
16. A medium composition as in claim 15 wherein the non-yellowing thermoplastic resin is present in an amount of about 300-500 parts by weight.
17. A medium composition as in claim 16 wherein the plasticiser is present in an amount of from 33 to 80 parts by weight.
18. A medium composition as in claim 17 wherein the plasticiser is an epoxidized oil.