The Effect of Dissolved Transition Metal Complexes on the Rate of Yellowing of Linseed Oil

Zhong Chen[1] **and Patrick E. Hoggard***
Department of Chemistry, Santa Clara University, Santa Clara, California 95053

ABSTRACT: A number of metal complexes were examined as potential antiyellowing additives for linseed oil-based coatings. Yellowing was measured as the rate of increase of the absorbance at 400 nm of solutions of 20% linseed oil in toluene. Most metal complexes increased the yellowing rate, but 1,1-bis(diphenylphosphino)ferrocene retarded the rate by 50% over a wide concentration range, and some complexes caused nonlinear changes that might make them useful as additives.

Paper no. J8960 in *JAOCS 76*, 279–282 (February 1999).

KEY WORDS: Autoxidation, linseed oil, transition metal complexes, yellowing.

The yellowing of linseed oil, and other oils containing linolenic acid, as a result of autoxidation has a significant effect on the use of linseed oil in coatings. Yellowing is thought to result from the introduction of carbonyl groups and the rearrangement of carbon–oxygen and carbon–carbon bonds into conjugated chains (1–5), which may possibly incorporate pyrroles, through reaction with molecular nitrogen (6). Autoxidation is a free-radical process that proceeds at a slow rate because of the relative immobility of the fatty acid chains in media of high viscosity. This is primarily a problem for indoor coatings, because sunlight prevents, and even reverses, yellowing (7).

In considering solutions to the problem of yellowing, the useful life of the coating is of primary importance. To retard the yellowing of coatings by a factor of 10 would virtually eliminate the problem because there would then be little observable change during the life of the coating. For similar reasons, an additive that might accomplish this retardation need not function catalytically. It is enough if it is consumed but will outlive the coating.

A number of compounds have been found to retard the oxidation of fats and fatty acids (8), but few investigations of compounds as additives for the potential retardation of yellowing have been done (2). In this paper, we examine the effects of several transition metal complexes on the yellowing of linseed oil. Because compounds of transition metals are commonly used in driers, which accelerate polymerization but also oxidation, leading to greater yellowing tendencies (9,10), transition metal complexes are perhaps not the first class of compounds that one might suspect of harboring retardation agents.

Metal ions can increase the rate of autoxidation by reacting with oxygen to yield peroxy radicals, or by reacting with already formed hydroperoxides.

$$\mathrm{ROOH} + M^{2+} \rightarrow [M(\mathrm{III}) - \mathrm{OH}]^{2+} + \bullet\mathrm{OR} \qquad [1]$$

On the other hand, metal complexes that can be readily oxidized can scavenge free radicals; for example,

$$M\mathrm{L}_n + \mathrm{R}\bullet \rightarrow M\mathrm{L}_n^{+} + \mathrm{R}^{-} \qquad [2]$$

Several factors may affect the ability of a metal complex to function in this way, most obviously oxidation potential but also coordinative unsaturation and the lability of the other ligands. Alternative scavenging possibilities include

$$M\mathrm{L}_n + \mathrm{R}\bullet \rightarrow M\mathrm{L}_{n-1}\mathrm{R}^{+} + \mathrm{L}^{-} \qquad [3]$$

and

$$M\mathrm{L}_n + \mathrm{R}\bullet \rightarrow M\mathrm{RL}_n \qquad [4]$$

A metal complex that scavenges radicals, retarding autoxidation and thus yellowing, might not be a good additive for a coating, because it may also retard polymerization. However, a metal complex may retard yellowing by acting after the oxidation step. Yellowing occurs as a result of rearrangement, which is temperature sensitive but reversible by low-wavelength light. Intramolecular rearrangements can sometimes be retarded by coordination to a metal, which can reduce the mobility of atoms that must move, and can alter electron densities in areas where double bonds must shift.

In this paper, we have examined only the effect of metal complexes on the yellowing of linseed oil, not any concomitant effects on polymerization rates.

EXPERIMENTAL PROCEDURES

Boiled linseed oil was obtained from Sigma Chemical Co. (St. Louis, MO) and contained 0.5% lead naphthenate as supplied. Toluene and the metal complexes were obtained from Aldrich

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[1] Present address: Department of Chemistry, Teacher's College, Yangzhou University, Yangzhou 225002, China.

*To whom correspondence should be addressed. E-mail: phoggard@scu.edu

Chemical Co. (Milwaukee, WI) or Strem Chemicals (Newburyport, MA), except tris(diethyldithiocarbamato)iron(III) and bis(diphenyldithiolene)nickel, $Ni(S_2C_2Ph_2)_2$, which were prepared by literature methods (11,12).

The measurement of yellowing was approximated through the absorbance of solutions at 400 nm for dilute solutions of linseed oil in toluene, or at 500 nm for neat linseed oil or high concentrations of linseed oil in toluene, for which the absorbance at 400 nm was too great. Visible spectra were recorded on a Shimadzu UV-160A spectrophotometer (Kyoto, Japan), with cells thermostatted at 20°C. In a typical yellowing experiment, an amount of a transition metal complex was weighed and then dissolved in toluene. Linseed oil (2 mL) was added to a 10-mL volumetric flask, a specific volume of the toluene solution of the metal complex was added, then the remainder of the 10 mL was made up with toluene. A 3.0-mL aliquot was transferred to a 1.0-cm quartz cuvette. The absorbance of the solution at 400 nm was measured periodically, and the solution was then immediately returned to dark storage. A qualitative perception of the depth of yellow color was also noted, which was consistent with the absorbance measurements. To reduce the possible acceleration of yellowing reactions by active sites on the quartz surface, cuvettes were treated with $Si(CH_3)_2Cl_2$, but little change in the rates was noted as a result.

Each concentration of each metal complex was run at least twice. The absorbance at 400 nm was plotted against time. When the variation with time was approximately linear, the slope, $\Delta A/\Delta t$, was used to represent the rate of yellowing. In some situations the variation with time was not linear, and the rate of yellowing could be represented by the instantaneous slope but varied throughout the observation period.

RESULTS AND DISCUSSION

Linseed oil was diluted with toluene to speed the yellowing process and permit more experiments to be done. The rate of yellowing of pure linseed oil as a function of dilution by toluene was tested. Figure 1 shows the variation of $\Delta A/\Delta t$ at 500 nm with linseed oil concentration for samples stored in the dark. The empirical asymmetric curve superimposed on the data was suggested by the approximately linear variation of $\Delta A/\Delta t$ (at 400 nm) observed for linseed oil concentrations in the range of 2–15%.

The variation of $\Delta A/\Delta t$ with linseed oil concentration was dramatically different for samples stored in the dark and in room (fluorescent) light, illustrated in Figure 2. At low linseed oil concentrations, yellowing, measured at 400 nm, was actually faster when samples were continuously exposed to light. Increasing the linseed oil concentration reduced the yellowing rate of light-exposed samples in contrast to the increase in rate for dark samples.

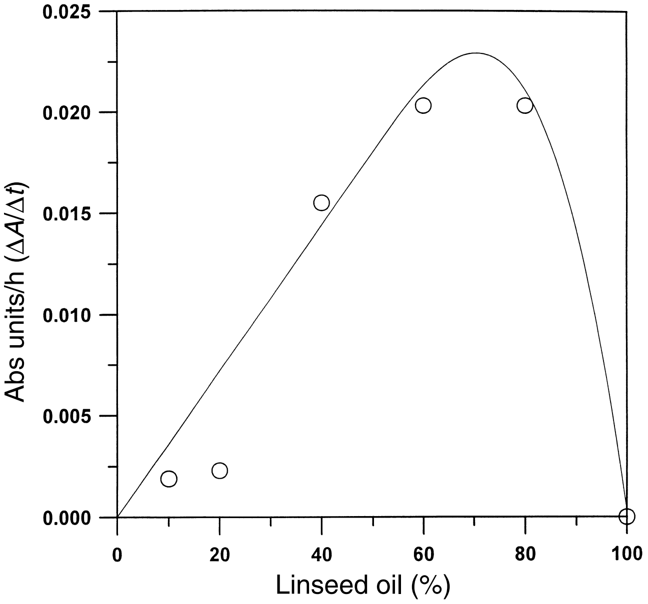

FIG. 1. Rate of yellowing of linseed oil–toluene mixtures, measured as the rate of increase of the solution absorbance at 500 nm for solutions stored in the dark. The curve consists of two separate quadratic functions joined at the maximum.

Complexes of several different transition metals were tested in 20% linseed oil in toluene to determine their effects on the rate of yellowing, measured as $\Delta A/\Delta t$ at 400 nm. Table 1 summarizes the results. With no complex added, the average observed rate was 5.19×10^{-3} absorbance units per hour. Almost every metal complex added increased the rate, some quite substantially. In most samples there was little relationship between the amount of the metal complex added and the

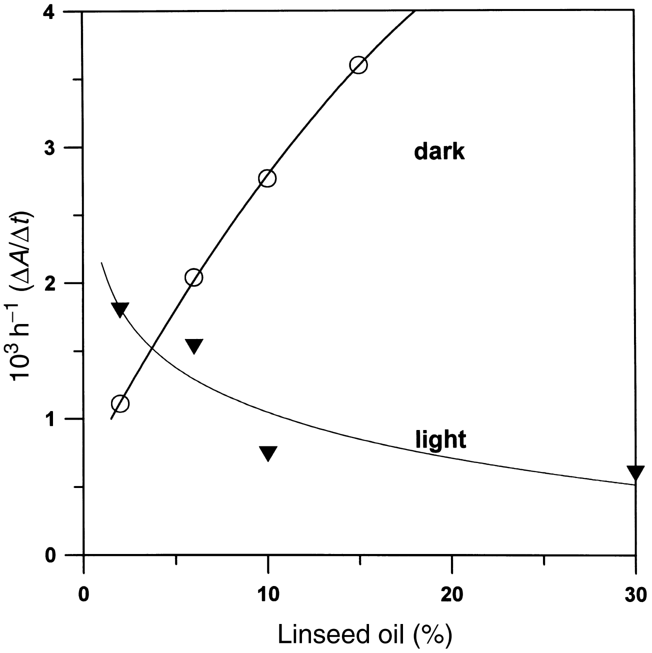

FIG. 2. Rate of yellowing of linseed oil–toluene mixtures, measured as the rate of increase of the solution absorbance at 400 nm for solutions stored in the dark (○) and in room (fluorescent) light (▼). The curves are logarithmic fits.

TABLE 1
Observed Yellowing Rates of 20% Linseed Oil in Toluene, Measured as $\Delta A/\Delta t$ (in absorbance units/h) at 400 nm, in the Presence of Dissolved Transition Metal Complexes

Complex	Amount^a (g)	Rate (10^{-3} h^{-1})
None	0.0	5.19 ± 0.52
Chromium(III) acetylacetonate	0.0013	15.3 ± 2.1
	0.0025	23.2 ± 13.5
	0.0064	26.2 ± 4.9
Chromium(III) 2-ethylhexanoate	0.0027	11.8 ± 0.8
	0.0088	17.2 ± 2.6
	0.0119	15.7 ± 0.7
	0.0137	12.1 ± 0.4
	0.0145	12.6 ± 1.3
	0.0204	20.2 ± 0.6
Cobalt(II) acetylacetonate	0.0013	14.8 ± 3.4
	0.0020	14.2 ± 4.5
	0.0031	18.2 ± 3.7
Bis(cyclopentadienyl)cobalt(III) hexafluorophosphate	0.0014	13.8 ± 2.2
	0.0044	8.6 ± 6.6
	0.0056	9.2 ± 0.4
Trimethylphosphinegold(I) chloride	0.0010	7.3 ± 1.1
	0.0033	5.8 ± 0.4
	0.0075	10.8 ± 1.5
Carbonylchlorobis (triphenylphosphine)iridium(I)	0.0010	12.0 ± 4.1
	Various	Nonlinear
1,1-Bis(diphenylphosphino)ferrocene	0.0010	2.1 ± 1.0
	0.0018	2.2 ± 0.7
	0.0041	2.3 ± 1.0
	0.0090	2.1 ± 0.4
	0.0165	2.4 ± 0.8
	0.0252	2.4 ± 0.4
	0.0420	2.9 ± 0.7
Tris(diethyldithiocarbamato)iron(III)	Various	Nonlinear
Tris(2,2′-bipyridine)iron(III) hexafluorophosphate	0.0035	Nonlinear
Bis(tetraethylammonium) tetrachloromanganate(II)	0.0019	12.6 ± 0.5
	0.0032	12.7 ± 1.0
	0.0064	13.0 ± 1.5
Dichloro[1,2-bis (diphenylphosphino)ethane]nickel(II)	0.0008	10.9 ± 4.9
	0.0011	5.2 ± 1.3
	0.0012	16.0 ± 1.4
	0.0016	3.5 ± 0.6
	0.0027	11.0 ± 0.6
	0.0035	5.2 ± 2.3
Bis(diphenyldithiolene)nickel	Various	Nonlinear
Tetrakis(triphenylphosphine)nickel	0.0010	13.5 ± 1.3
	0.0023	11.6 ± 2.4
	0.0033	14.9 ± 5.9
Nickel(II) 2-ethylhexanoate	0.0018	16.7 ± 0.5
	0.0073	16.2 ± 2.2
	0.0119	20.0 ± 1.8
Triosmiumdodecacarbonyl	Various	Nonlinear
(±)di-μ-chlorobis{2-[(dimethylamino)methyl]phenyl-C,N} dipalladium	0.0008	29.1 ± 1.5
	0.0019	40.0 ± 4.7
	0.0032	50 ± 25
cis-Bis(benzonitrile)dichloroplatinum(II)	0.0014	11.3 ± 0.5
	0.0022	20.1 ± 0.4
	0.0038	11.3 ± 0.4
cis-Dichlorobis(pyridine)platinum(II)	Various	Nonlinear
trans-Dichlorobis (triphenylphosphine)platinum(II)	0.0014	6.6 ± 0.8
	0.0034	8.0 ± 0.4
	0.0064	6.6 ± 0.8
cis-Dichlorobis (triphenylphosphine)platinum(II)	0.0011	9.9 ± 3.3
	0.0022	10.2 ± 2.8
	0.0030	10.1 ± 1.9
Dichlorobis(ethylenediamine) platinum(II)	0.0012	14.9 ± 4.4
	0.0015	11.7 ± 0.6
	0.0018	11.5 ± 5.2
	0.0033	12.3 ± 1.2
Potassium trichloro(ethylene) platinate(II) hydrate	0.0014	19.8 ± 3.7
	0.0031	24.4 ± 1.3
	0.0038	29.4 ± 1.2
Chlorotris(triphenylphosphine) rhodium(I)	0.0012	15.2 ± 0.4
	0.0022	18.8 ± 12.2
	0.0031	24.1 ± 9.8
Bis(cyclopentadienyl)ruthenium	0.0012	9.8 ± 4.0
	0.0018	12.0 ± 2.9
	0.0030	14.2 ± 3.3
	0.0032	7.7 ± 1.1
	0.0113	31.3 ± 0.5
	0.0124	12.3 ± 5.9
Bis(pentamethylcyclopentadienyl) ruthenium	0.0010	9.0 ± 1.6
	0.0026	9.6 ± 0.8
	0.0112	11.6 ± 1.1
Tetraethylammonium bis(acetonitrile) tetrachlororuthenate(III)	0.0014	11.5 ± 5.4
	0.0036	12.3 ± 4.1
	0.0063	16 ± 15
Trirutheniumdodecacarbonyl	0.0025	14.7 ± 1.8
	0.0051	17.9 ± 1.8
	0.0113	31.7 ± 9.8
Ytterbium(III) hexafluoroacetylacetonate dihydrate	0.0016	21.7 ± 10.5
	0.0030	10.9 ± 0.4
	0.0060	29.2 ± 5.1

[a] In 2.0 mL linseed oil + 8.0 mL toluene.

observed yellowing rate, and this exposed an undesirable inconsistency in some instances, notably for dichloro[1,2-bis(diphenylphosphino)ethane]nickel.

For most of the complexes studied, the increase in absorbance was approximately linear with time over the approximately 7-h test period. Others yielded nonlinear behavior, as noted in Table 1. Typically, this occurred when the complex itself absorbed enough 400 nm light to raise the starting absorbance significantly. An initial drop in absorbance, probably due to a reaction of the metal complex with radicals already present from the linseed oil, was then followed by a gradual rise. If the initial absorbance drop was brief, the yellowing rate was calculated from the subsequent linear variation of absorbance with time.

Chromium(III) and nickel(II) ethylhexanoate salts, which are used as driers, were included in the study. They both caused three- to fourfold acceleration of the yellowing rate, as might be expected. A few metal complexes caused even greater acceleration, especially the chlorine-bridged dinuclear palladium complex, which accelerated the yellowing rate tenfold at the highest concentration used.

One complex, 1,1-bis(diphenylphosphino)ferrocene, consistently retarded the yellowing process by about a factor of

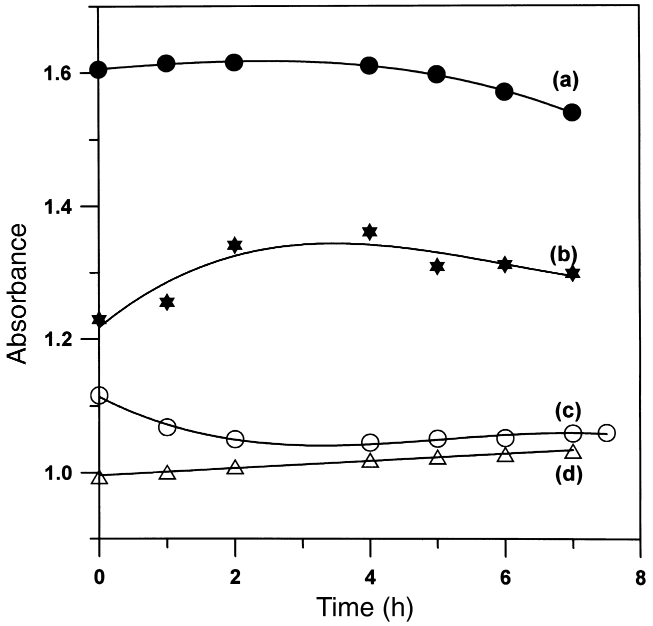

FIG. 3. Absorbance at 400 nm as a function of time of solutions of 20% linseed oil in toluene containing (a) bis(dithiobenzil)nickel (●); (b) triosmium dodecacarbonyl (✶); (c) tris(bipyridine)iron(III) hexafluorophosphate (○); (d) nothing (△).

two, regardless of concentration. The mechanism by which retardation takes place is not evident.

The nonlinear behavior seen with some of the complexes is illustrated in Figure 3, compared to a linseed oil (20%) blank. These complexes may be potentially useful as retardation additives. Triosmium dodecacarbonyl initially exhibited an increase in the absorbance at 400 nm, but this was followed by a gradual decrease. Bis(dithiobenzil)nickel solutions increased slightly in absorbance at 400 nm for the first 2 h, but the absorbance declined substantially thereafter. Bis(dithiobenzil)-nickel is used as a dye and has an intense emerald green color, which, when used at low concentrations, tends to make the yellow from the linseed oil less noticeable. If the rate of yellowing of the linseed oil is also retarded, which is not certain from the data, this compound may be a useful additive for linseed oil-based coatings. Another compound studied, tris(diethyldithiocarbamato)iron(III), behaved similarly. It has a strong blue color that also tends to mask the yellow from linseed oil when used in small concentrations.

Although most metal complexes accelerate the yellowing process in linseed oil/toluene solutions, some are potentially useful as antiyellowing additives in linseed oil-based coatings. Perhaps the best candidate is 1,1-bis(diphenylphosphino)ferrocene, which consistently reduced the rate of yellowing, judged by absorbance at 400 nm, by a factor of two, even at quite low concentrations.

ACKNOWLEDGMENT

This work was supported by USDA CSREES Grant No. 94-37500-1298.

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[Received August 3, 1998; accepted October 6, 1998]