ABSTRACT

A high degree of whiteness in coated papers is necessary for a quality image. Such papers often yellow in their storage environment. This work studied the influence of daylight radiation and nitrogen oxide gas on the yellowing of coated papers. The yellowing is due to the action of nitrogen oxide on antioxidants in latexes and fluorescent agents. Ammonia intensifies yellowing caused by nitrogen oxide acting on latexes but not on fluorescent agents.

Application: *NO_2 is the main cause of yellowing. NH_3 intensifies the yellowing it produces.*

Yellowing of coated papers under the action of heat, daylight radiation, and nitrogen oxide gas

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IN A PREVIOUS STUDY (1), WE established the presence of NO_2 in the environment of some coating machines from the transformation of ammonium hydroxide—a component of some coating colors—into nitrogen oxide in the burners of hot air supply systems.

Coated papers are sensitive to their surroundings and may yellow. In this work, we investigate the effect of daylight and the presence of certain gases like NO_2 and NH_3 coming from the use of ammonium hydroxide in coating colors and the drying system for coated papers.

EXPERIMENTAL METHODS

Nature of products

The pigments used were ground calcium carbonate and kaolin of general use. The calcium carbonate with ISO brightness of 90 was whiter than the kaolin with an ISO brightness of 85. The particle size of calcium carbonate was smaller, and its distribution was narrower than the kaolin. For the calcium carbonate, 98% of the particles have a diameter lower than 2 µm compared to 80% for the kaolin.

The latexes used in this work were radical emulsion terpolymers of styrene, butadiene, and acrylic acid terpolymers *(2)*. **Table I** shows the composition and properties of the principal latex used.

Secondary products examined included fluorescent agents used as optical brighteners. A typical material was diamino-stilbene-sulfonic acid diluted in polyethylene glycol. **Figure 1** provides the chemical formula.

The amount of optical brighteners in coating colors must not exceed a certain threshold to avoid the phenomenon of grayness. Polyvinyl alcohol is the carrier for the optical brightener in the coating color.

It is important to note that the latex used in this work contained an antioxidant. This is contrary to most latex products used in the paper industry. The antioxidant contains hindered phenols. Figure 1B and 1C show the chemical formulas for typical antioxidants used in our latex *(3)*.

We applied the coatings in the laboratory and at a paper mill. The recipes were the same for both. Only the support varied. The support for the laboratory trials was a paper made in the mill from bleached chemical hardwood and softwood pulps. Its surface weight was 70 g/m^2. For the work in the paper mill, the support was a paper using bleached chemical pulp. It had a precoating of calcium carbonate and starch applied with a film press. Its surface weight was 100 g/m^2. **Table II** gives the color recipe. We adjusted the solids content of the coating color to 69% with water and adjusted the pH to 8.7 using ammonium hydroxide to avoid flocculation.

Sample preparation

We prepared the latex dried by lyophilization by putting the frozen solution of latex under vacuum for 24 h. The product obtained was very porous and had a large specific area. This characteristic improved the sensitivity of the optical measurement of yellowing after aging.

We made films of latex by spreading dispersions on thick aluminum foil with an applicator followed by drying for 36 h in ambient air in the dark. The films peeled from their foil had a thickness of approximately 300 µm. This thickness provided easy handling for significant optical measurements. Films with optical brighteners made the same way contained 20% silica grains of 60 µm by weight added to the initial dispersion to increase the light scattering.

To coat papers in the laboratory, we spread the color on the paper support with an applicator. The deposit was 14 g/m^2. Drying used an oven at 103°C for 2 min. Papers coated in the mill were manufactured in reels and then converted into sheets.

Analysis methods

Physico-chemical analyses. Extracting the latex with an appropriate solvent such as toluene or dimethyl formamide, we could isolate that part of the latex that did not crosslink. The extraction took place

in a Soxhlet for 24 h. After extraction, the samples underwent drying at ambient air without exposure to daylight followed by placing under vacuum. We performed infrared spectroscopic analysis on the samples during aging. A Biorad SPC 3200 apparatus provided the absorbance spectra.

Optical analyses. We measured optical properties after the latex films had yellowed. The scattered reflection spectra from 400–700 nm used a Datacolor 2000 spectrocolorimeter with measuring geometry of D, 0. A gloss trap excluded the specular component. There were measurements with and without ultraviolet (UV) light. The light source was a Xenon flash simulating D65 lighting. To obtain the scattered reflection spectra, the samples were on a white background with known optical characteristics. The reflection factor was similar to that of the coating color. Its value was 0.89 in the 400–700 nm range. In our research, the yellowing index (Y.I.) corresponded to that of the ASTM E 313 norm calculated from the trichromatic coordinates Y and Z as follows:

$$Y.I. = 100[1 - 0.847(Z/Y)] \quad (1)$$

$$Y = \int_{400}^{700} E_\lambda \overline{Y}_\lambda R_\lambda d\lambda \quad (2)$$

$$Z = \int_{400}^{700} E_\lambda \overline{Z}_\lambda R_\lambda d\lambda \quad (3)$$

where

λ = wavelength
E_λ = spectral energy flux of the source
$\overline{Y}$ = color matching function eye
$\overline{Z}$ = color matching function eye
R_λ = spectral reflection factor of the sample.

Because some samples were fluorescent, we analyzed with and without excitation of the fluoresence. Data shows Y.I. measured without UV and Y.I. measured with UV.

Initial monomer composition: 53% styrene, 45% butadiene, and 2% acrylic acid
Solids content: 50%
pH: 4.5
Brookfield viscosity: 150 mPa·s at 100 rpm
Surface tension: 56 $mN \cdot m^{-1}$
Average particle diameter: 0.15 µm
Glass transition temperature: -6 °C
Density: 1 g/cm^3

I. Composition and properties of principal terpolymer latex

For nonfluorescent samples, the values of Y.I. were positive, and they were negative for fluorescent samples. This allowed classifying the values for Y.I. in negatively decreasing values with a value of -1 more yellow than a value of –10. To compare the evolution with the initial state, we also measured relative variations of yellowing index, ΔY.I./Y.I.

Accelerated aging methods

Daylight radiation accelerated aging. Measurement of accelerated aging under conditions of daylight used two conditions in a Xenotest apparatus. This device has a Xenon lamp that reproduces daylight in its total radiation. The other condition used an anti-UV Kodak Wratten 2A filter providing filtered radiation. This filter absorbs radiation with wavelengths lower than 400 nm. During these experiments, the temperature over the samples was 35°C.

Accelerated aging by NO_2 and NH_3 gases. We made experiments for accelerated aging at 20°C without daylight in a simulator. The atmosphere had a relative humidity of 50% and contained 25 ppm NO_2 and 50 ppm NH_3.

We chose the amounts of NO_2 and NH_3 to increase the yellowing. Only 2 ppm NO_2 and 8-ppm NH_3 were present in the environment of the coating machine *(1)*. The duration of 24 h simulated the storage period of reels of coated papers before converting into sheets.

Component	Parts
Calcium carbonate	80
Kaolin	20
Terpolymer latex	8.8
Polyvinyl alcohol	0.2
Optical brightener	1.5
Calcium stearate	1
Dispersant	0.25

II. Recipe for the coating color used to prepare the coated paper

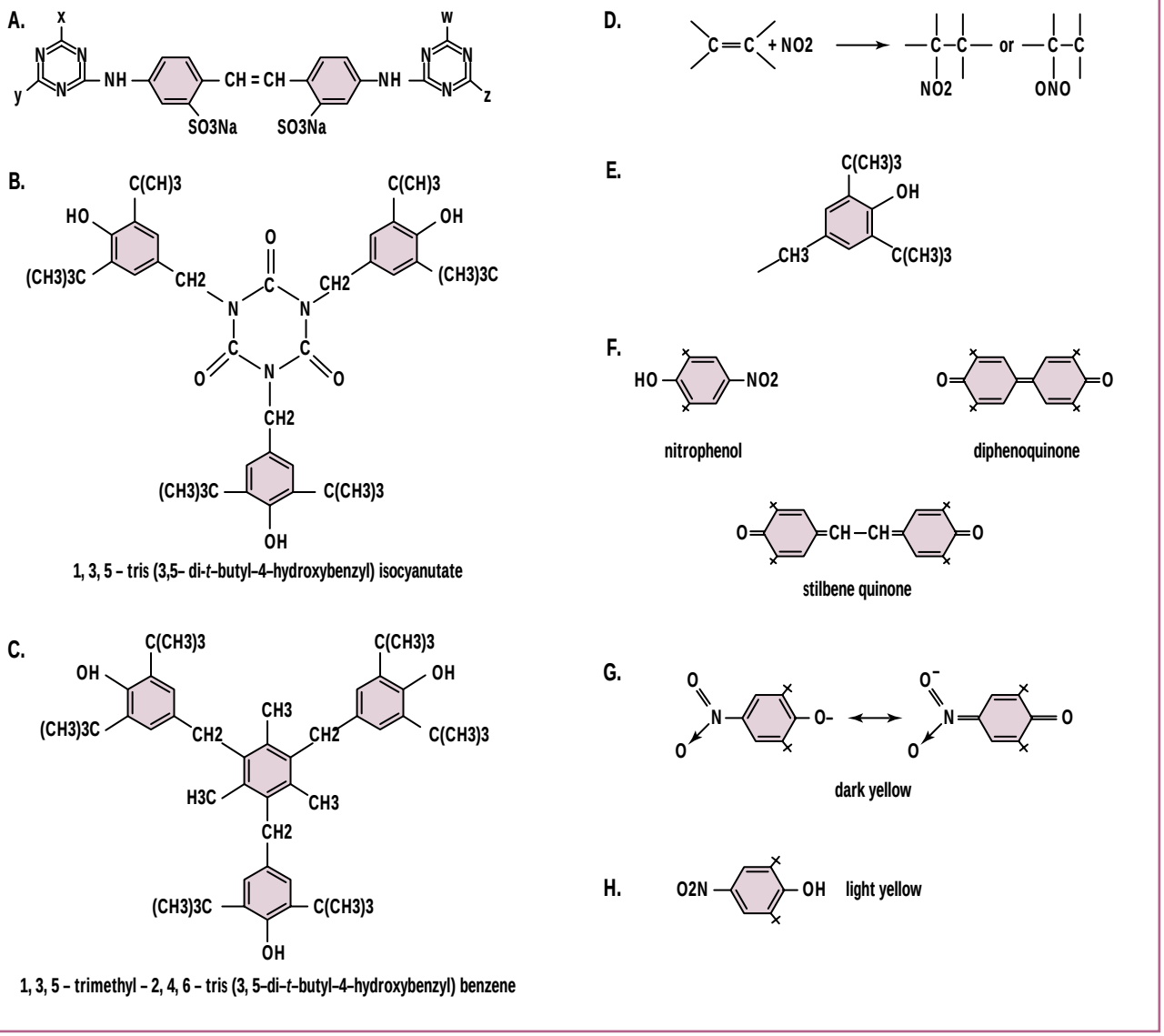
RESULTS AND DISCUSSION

Daylight accelerated aging of latex containing antioxidants

Films of terpolymer latex underwent exposure to the total daylight radiation, $\lambda > 300$ nm, or to the filtered radiation, $\lambda > 400$ nm. **Figure 2** shows the relative variations of the Y.I. for the latex over time. **Figure 3** gives the reflectance spectra of latex after 20 days accelerated aging. Comparisons are against an unaged film.

Analysis of the figures shows that only the UV radiation with $\lambda < 400$ nm is responsible for yellowing of the latex. Radiation with wavelengths higher than 400 nm leads to bleaching of the coated sheet. This can mask the effect of the yellowing caused by the prolonged exposure to heat at 35°C. The effect of daylight radiation with $\lambda > 300$ nm during an initial stage gives soft bleaching that is characteristic of the dominating action of the wavelengths higher than 400 nm. During a second stage, there is a yellowing due to the dominating action of the wavelengths smaller than 400 nm and prolonged exposure to heat. After a certain duration, the result is a yellowing phenomenon.

The comparison of reflectance spectra of unaged and aged films of latex clearly shows yellowing by higher absorption in the 400–470 nm region—blue color range. According to the color matching functions, λ and $\overline{Y}$ and the definition of Y.I., a lower reflectance in this field corresponds to a higher



1. Chemical formulas and reactions

value for Y.I. Examination of the blue color range can therefore provide an indication of the yellowing.

Comparison of daylight radiation and heat accelerated aging for the latex

We compared aging as a function of time in an oven at 70°C at 50% RH or in the Xenotest with or without the use of the UV filter for thin layers of the terpolymer latex without scattering pigments. **Figure 4** gives the relative variation of Y.I. as a function of time exposed to accelerated aging.

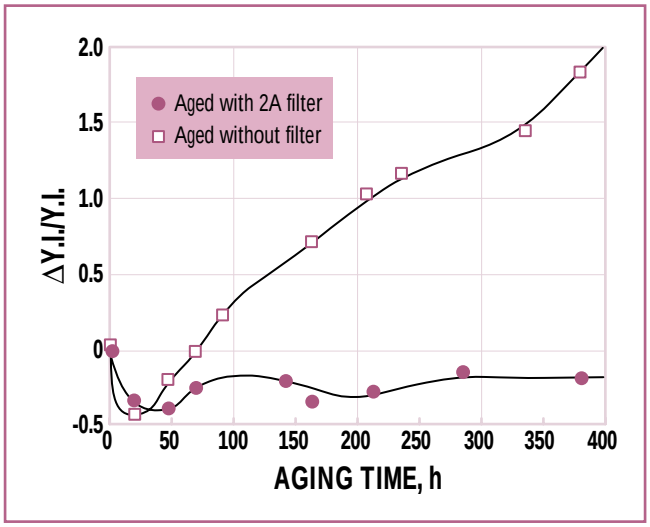
Analysis of the curves shows that the heat and humidity aging conditions in this work lead to significant yellowing of the latex compared to the bleaching action for the radiation with wavelengths higher than 400 nm and the yellowing action for the radiation with wavelengths lower than 400 nm. We conclude that the effect of heat and humidity prevails over that of total radiation of daylight in the accelerated aging conditions used here.

Daylight accelerated aging of coated papers

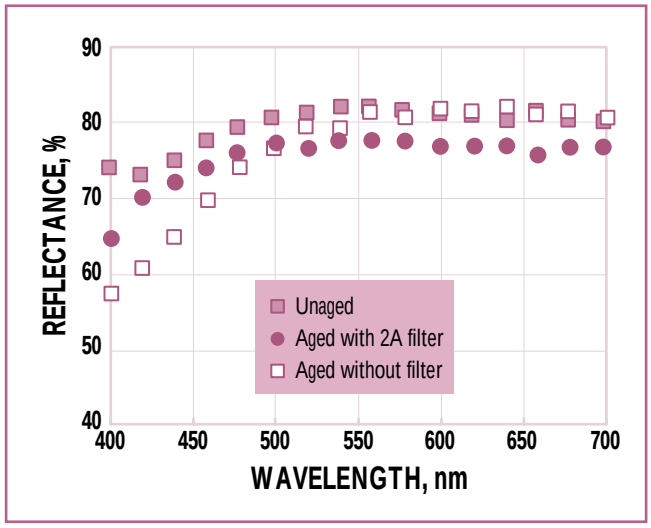
We exposed industrial coated papers under the radiation of the Xenotest with $\lambda > 300$ nm. **Figures 5 and 6** give the evolution of the Y.I. measured without or with UV over time for a glossy coated paper of 135 g/m^2 manufactured for rotogravure printing.

Analysis of these figures provides the following comments:

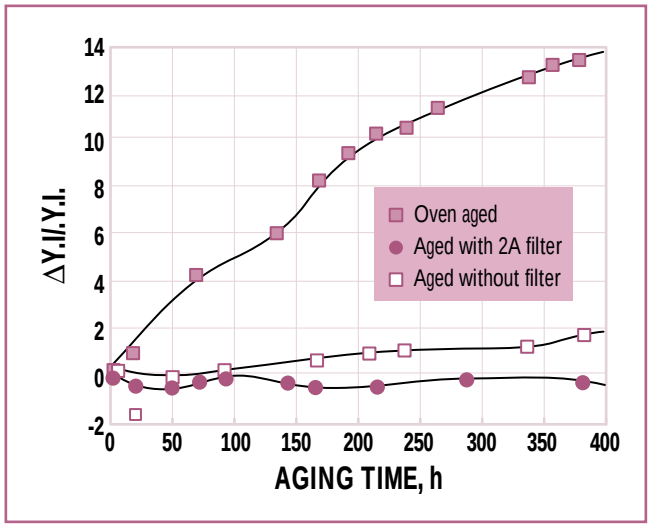
- For the analyses without UV, the action of the total radiation produces in the first hours a bleaching phenomenon with the latex. This is characteristic of the dominating action of the wavelengths higher than 400 nm. During a second stage, it causes yellowing by the dominating action of the wavelengths smaller than 400 nm and prolonged exposure to heat. These two phenomena of bleach-



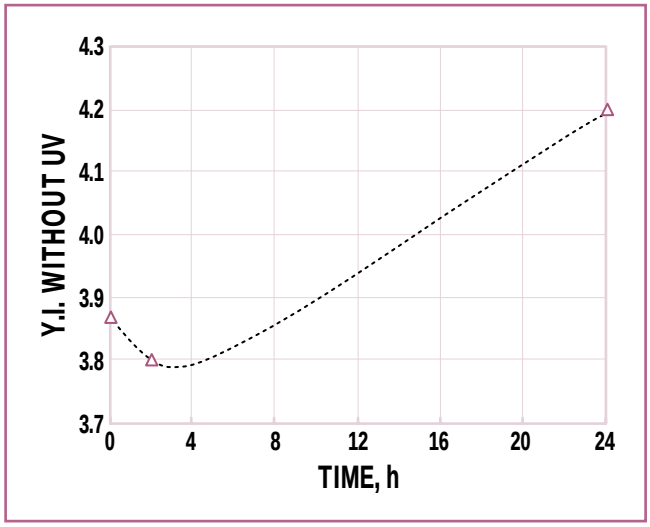
2. Relative variations of Y.I. for a film of terpolymer latex aged in a Xenotest with and without UV filter



3. Reflectance spectrum of a terpolymer latex film aged for 20 days in a Xenotest with and without UV filter



4. Comparison of aging in Xenotest with and without UV filter to oven aging at 70 °C and 50% RH



5. Y.I. evolution without UV excitation for a glossy coated paper 135 g/m² as a function of aging time in the Xenotest

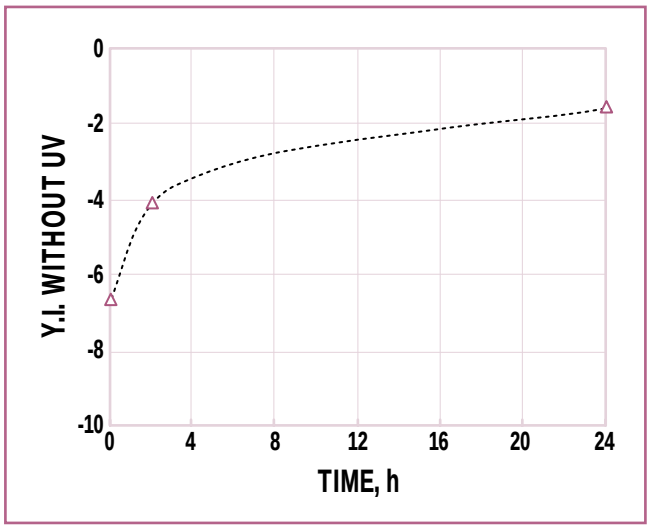
ing and yellowing are simultaneous. Above a certain time of aging, the action of yellowing is predominant. The effect of yellowing and bleaching may be reversible according to the spectral nature of the radiation lower or higher than λ = 400 nm, respectively, as observed elsewhere *(4, 5)*.

- A continuous increase of Y.I. characterizes the analyses with UV. These results show that the action of the radiation of wavelengths lower than 400 nm affects the optical brightener efficiency that decreases with the increasing aging.

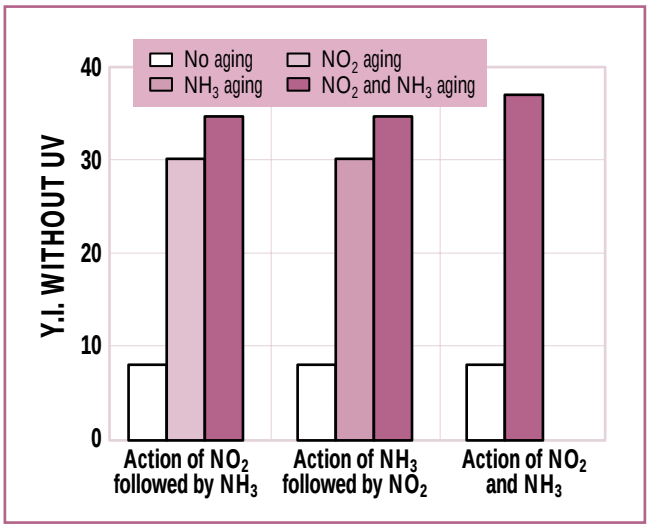
Accelerated aging of latexes under NO_2 and NH_3 gases

We performed accelerated aging in a simulation enclosure on lyophilized latexes. The evolution of the optical properties was more significant than on a film because of the porous and scattering texture. **Figure 7** shows the separate, successive, and simultaneous action of NO_2 and NH_3.

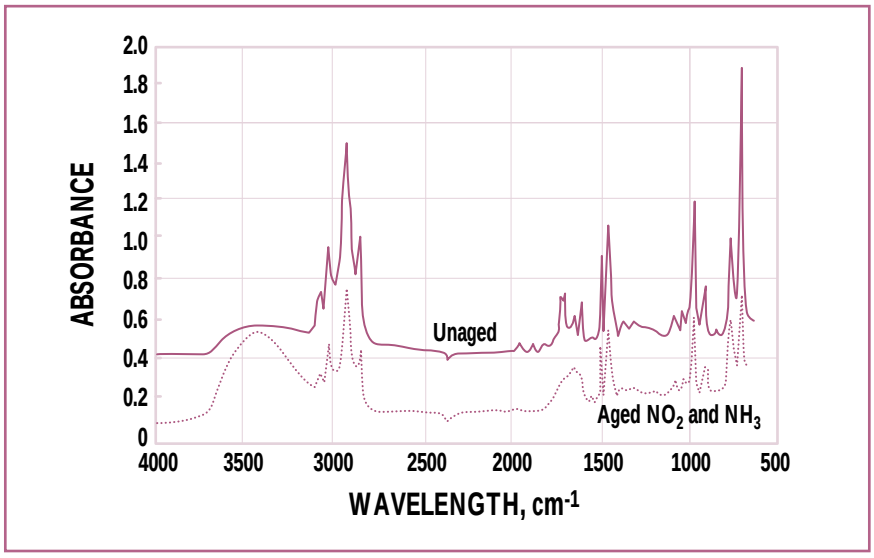
Analysis of the results shows that NO_2 alone leads to yellowing, NH_3 alone produces light bleaching, and NH_3 increases the yellowing produced at first by NO_2. NO_2 is the major culprit causing yellowing. The only effect of NH_3 is to intensify the yellowing produced by NO_2.



6. Y.I. evolution with UV excitation for a glossy coated paper 135 g/m² as a function of aging time in the Xenotest



7. Effect of NO_2 and NH_3 gases on the lyophilized terpolymer latex on the measurement of Y.I. without UV excitation



8. Infrared spectra of unaged and aged lyophilized terpolymer latex extracts in the presence of NO_2 and NH_3

We extracted sol fractions of the lyophilized latexes with toluene before and after aging. **Figure 8** shows the infrared spectra of these sol fractions or extracts using the conditions described above. The spectra of this figure indicate the following:

- There is an increase of the absorbance in the 3600–3100 cm^{-1} region characteristic of hydroxy and amino groups. If we consider the absorbance at 3430 cm^{-1}, we observe that after aging the peak intensity is multiplied by 5 compared to the reference at 758 cm^{-1}. This is characteristic of styrene that is not supposed to yellow.
- There is an increase of the absorbance in the 1750–1600 cm^{-1} region characteristic of the formation of carbonyl and nitro groups. Nitroso products, C–NO, occur in the region of 1650–1600 cm^{-1} and nitrite products, O–NO, occur in the region of 1680–1650 cm^{-1}. If we consider the absorbance at 1640 cm^{-1} after aging compared with that of the reference peak at 758 cm^{-1}, the value doubles.

Analyses by stearic exclusion chromatography and mass spectrometry on lyophilized latex extracts did not show detectable differences before and after aging. Only a small quantity of species is responsible for the yellow coloration. It is not easy to detect such trace amounts.

Nitration of the latex by NO_2 could occur on the unsaturated carbon atoms of the polymer with formation of nitro derivatives according to the reaction (D) of Fig. 1. The probability of this reaction that needs high temperature, UV light, and specific unsaturated structures is low in our experimental conditions. The resulting products from the reaction are not yellow unless they combine with carbonyl groups. We do not consider this reaction a

likely possibility.

As shown by Wagner *(6)* and Smeltz *(7)*, NO_2 reacts with 4-methyl-2,6-di-*tert*-butylphenol (BHT) to form yellow stilbene quinone derivatives or diphenoquinones. The antioxidant in this work could provide the phenolic starting product, BHT, for the reaction with NO_2.

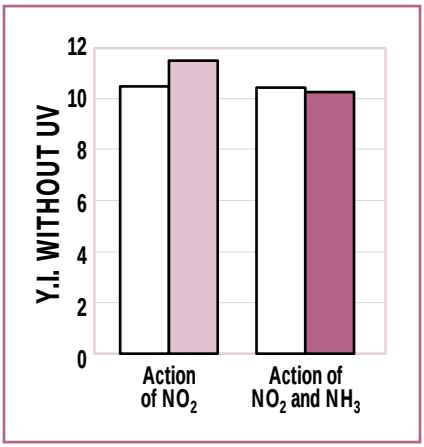
During the decomposition of antioxidants, the phenolic function (E) of Fig. 1 splits away, and the BHT can then react with NO_2 as Smeltz notes *(7)* to form the yellow derivatives. BHT can also originate as a separate entity in the antioxidant before the decomposition occurs and can promote the yellowing reaction to nitrophenol, diphenoquinone, and stilbene quinone shown as F in Fig. 1.

Pospisil *(8, 9)* proposed the mechanisms of formation of these products when he studied the undesired reactivity of phenol—generally used as a primary chain breaking antioxidant—with environmental pollutants.

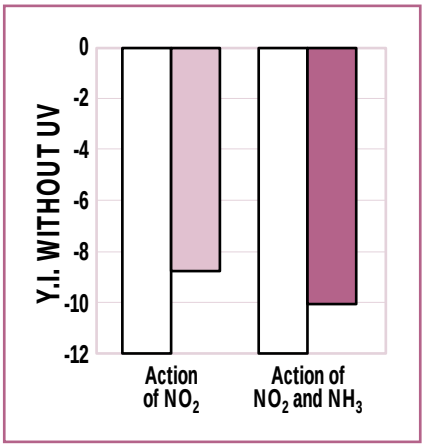
NO_2 acts as an oxidation agent and leads to the formation of phenoxy radicals. Either nitrophenol and diphenoquinone can form, or C–C coupling reactions from mesomeric structures of phenoxy radicals can lead to stilbene quinone derivatives.

Other researchers *(10)* investigated the use of NO_2 in pulp delignification because of its high reactivity toward lignin that contains many phenolic groups. In this sense, NO_2 is like ClO_2. These studies observed the formation of colored quinone derivatives—normally eliminated from the pulp by solubilization.

Wagner *(11)* has explained the more intense coloration obtained in the presence of NH_3 using tautomerization in which benzoide products turn into quinoides as G of Fig. 1 shows. Without NO_2, there is a light yellow color due to the presence of the chemical product H in Fig. 1.



9. Effect of NO_2 and NH_3 gases on the Y.I. measured without UV excitation for an optical brightener film containing 20% silica by weight



10. Effect of NO_2 and NH_3 gases on the Y.I. measured with UV excitation for an optical brightener film containing 20% silica by weight

Accelerated aging of optical brighteners

Figures 9 and 10 show the results of accelerated aging of optical brighteners under NO_2 and NH_3 in a simulation enclosure. The figures indicate a yellowing of optical brighteners and a decrease in their fluoresence under the action of NO_2 alone. NH_3 does not increase the yellowing as with the latex but decreases it.

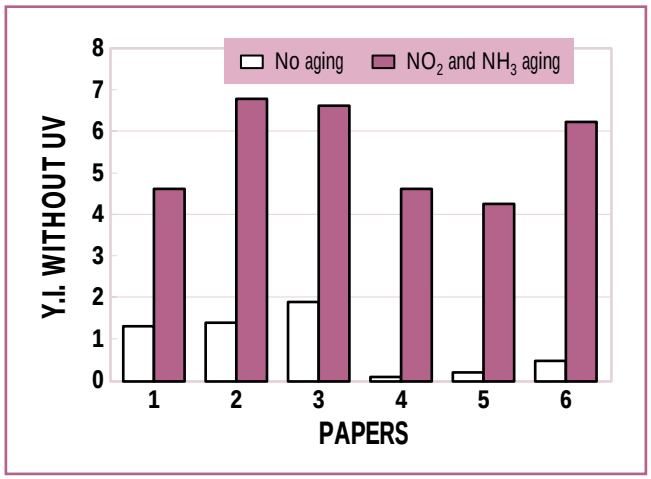
In an optical brightener solution, addition of antioxidant products stabilizes the polymer acting as a carrier. The yellow coloration could result here only from the formation of stilbene quinone derivatives, because the yellow coloration did not increase in the presence of alkali.

Accelerated aging of coated papers

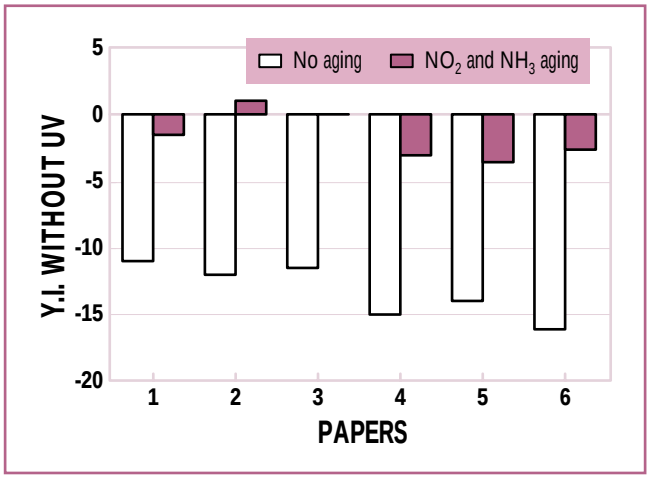
We concluded this work by studying the NO_2 and NH_3 influence while varying the amount of latex and pigments of coated papers. Several coated papers made in the laboratory used different proportions of latex and pigments as **Table III** shows. The aging conditions in the simulation enclosure were the same as described previously. **Figures 11 and 12** show the variations of the Y.I. during aging. **Tables IV and V** show the variation of Y.I., after aging for these coated papers using measurements with or without UV excitation.

Comparison of these coated papers containing different amounts of pigments and latex prepared in the laboratory leads to the following comments:

- The presence of kaolin gives a higher Y.I. Figures 11 and 12 show that the Y.I. values are higher for coated papers containing kaolin than for coated papers containing only calcium carbonate. This remark remains valid after aging with the gases, although Tables IV and V show that ΔY.I. after aging may sometimes be smaller for coated papers containing kaolin. These trends arose from considering an estimated error for the measurement value of Y.I. of 0.2.
- For papers coated with 100 parts calcium carbonate, yellowing increases with the amount of latex that contains antioxidant. It relates to the antioxidant present rather than to the latex itself.
- For papers coated with 80 parts calcium carbonate and 20 parts kaolin, we noticed a minimum of yellowing for latex at 8.8 parts. With electron scanning microscopy, we observed that this corresponds to a nonhomogeneous and porous coating layer structure *(12)*. The decrease in yellowing could result from an intensified scattering produced by the porosity of the layer.



11. Effect of NO_2 and NH_3 gases on the Y.I. measured without UV excitation for papers coated in the laboratory with various amounts of terpolymer latex and pigments



12. Effect of NO_2 and NH_3 gases on the Y.I. measured with UV excitation for papers coated in the laboratory with various amounts of terpolymer latex and pigments

Paper number	Calcium carbonate, parts	Kaolin, parts	Latex, parts
1	80	20	8.8
2	80	20	6.0
3	80	20	12.0
4	100	-	8.8
5	100	-	6.0
6	100	-	12.0

III. Coated papers

Parts of latex containing antioxidant	ΔY.I. after aging 24 h without UV	ΔY.I. after aging 24 h with UV
6	+4.1	+10.9
8.8	+4.5	+11.6
12	+5.8	+13.2

IV. Variations of the Y.I. during aging with NO_2 and NH_3 for coated papers using calcium carbonate (4, 5, and 6)

Parts of latex containing antioxidant	ΔY.I. after aging 24 h without UV	ΔY.I. after aging 24 h with UV
6	+5.7	+12
8.8	+4.0	+9.0
12	+5.4	+10.7

V. Variations of the Y.I. during aging with NO_2 and NH_3 for coated papers based on calcium carbonate and kaolin (1, 2, and 3)

SUMMARY

This study concerned the yellowing of antioxidants used with latexes and fluorescent agents used in coating colors under exposure to heat, humidity, daylight radiation, and NO_2 and NH_3 gases. Our work led to the following conclusions:

- Yellowing of coating layers is due to the presence of antioxidants contained in the latex and to the use of fluorescent agents.
- The effect of daylight radiation gives two forms of photochemical action. The effect of wavelengths lower than 400 nm is a yellowing of coated papers. The effect of visible light, $\lambda > 400$ nm, is a bleaching of the material.
- The effect of NO_2 on the antioxidant of a latex that contains hindered phenolic products leads to pronounced yellowing. The formation of nitro derivatives such as nitrophenol, diphenoquinone, and stilbene quinone causes the discoloration. NH_3 is inert toward the terpolymer latex studied, but it intensifies the yellowing caused by NO_2.
- NO_2 also leads to the yellowing of fluorescent agents and to the concomitant decrease of the fluoresence efficiency. Contrary to

KEYWORDS

Coated papers, color reversion, day light, electromagnetic radiation, light, nitrogen compounds, nitrogen oxides, oxides, paper grades, radiation, reversion, thermal properties, thermal stability, yellowing.

the case of the latex, NH_3 does not intensify the yellowing. **TJ**

At the time this paper was written, Mailly was research engineer at Laboratoire Génie des Procédés Papetiers; she is now product manager of graphic paper at Arjo Wiggins. Serra Tosio and Silvy are professors at Laboratoire Génie des Procédés Papetiers, Ecole Française de Papeterie et des Industries Graphiques, BP 65, 38402 Saint Martin d'Hères cedex, France.

The authors thank P. Lepoutre (University of Maine), R. L. Van Gilder (Dow Chemical Co.), and A. Gandini (National Polytechnic Institute of Grenoble) for assistance and technical discussions.

Received for review March 6, 1996.

Accepted Sept. 16, 1996.

Presented at the TAPPI 1996 Coatings Conference.

LITERATURE CITED

1. Mailly, V., "Contribution à l'étude de la permanence des propriétés optiques des papiers couchés," Thèse de Doc torat, Institut National Polytechnique de Grenoble, Grenoble, France, 1994.
2. Heiser, E. J. and Faulakis, F., in *Pape Coatings TAPPI Monograph series no. 37* (A. R. Sinclair, Ed.), TAPPI PRESS, Atlanta, 1974, p. 22.
3. Anon., *Index of Commercial Antioxidants & Antiozonants*, 4th edn., Goodyear Chemical Co., Akron.
4. Le Nest, J. F., Silvy, J., and Gandini, A., *J. Photochem.* 31:359(1985).
5. Silvy, J. and Le Nest, J. F., *Mise en évidence par diffusion de la lumière d'un effet photochrome de la cellulose*, C. R. Acad. Sc., Paris, t. 271, 1970, p. 221.
6. Wagner, H., *Melliand Texilberichte* 63(4): 291(1982).
7. Smeltz, C., *Textile Chemist and Colorist* 15(4): 17(1983).
8. Pospisil, J., *Polymer Degradation and Stability* 399: 103(1993).
9. Pospisil, J., *Polymer Degradation and Stability* 40: 217(1993).
10. Gierer, J., *Holzforschung* 36(4): 55(1982).
11. Wagner, H., *Textil Praxis International* 355(1983).
12. Lepoutre, P. and Rezanovich, A., *Tappi* 60(11): 86(1977).