

Migration of metals through linerboard: an exploratory study

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ABSTRACT: *Corrugating adhesive prepared with flexographic wash water may contain metal compounds or complexes. For some purposes, these metals must remain in situ; that is, they must not migrate from the glue line through the linerboard to the product in the container. This exploratory study examined metal migration behavior under the influence of an isothermal moisture gradient. Movement of metals, as indicated by a concentration build-up near the outer surface of the linerboard, was not found. The concentrations of metals contained in the commercial wash water supplied for this study were small compared to that of the background metals in the linerboard. These background metals also masked any introduced metals.*

KEYWORDS: *Corrugated boards, fiber boards, flexography, liner board, metals, migration, starch, wash waters.*

Using flexographic wash water in corrugated fiberboard starch adhesive is a relatively new practice. Because this water may contain metal compounds and complexes (hereafter referred to simply as metals) from the ink, there is concern that such metals might migrate from the glue line through the linerboard to the board's surface. Linerboard contact with the container's contents then might allow metal migration to the package's contents.

Several authors (1-13) have studied metal migration out of packaging

materials, with Knezevic (1-6) apparently being the most involved. From this literature, one finds that while metals can be made to migrate, usually under acidic conditions, there appears to be a minimal health risk from metals transferring to products from the packaging (2-5, 8, 10, 11). However, in all of these works there is little information on the movement, if any, of metals within the paperboard to the surface in contact with the product. Therefore, there is still a concern that any potential addition of metals to corrugated fiberboard, such as by using flexographic wash

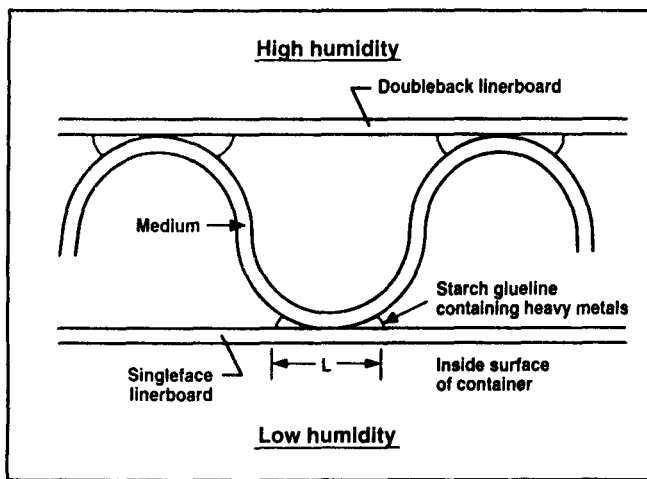
water for preparing the starch adhesive, could affect products in contact with the linerboard.

This study was designed to examine the potential for metal migration by subjecting a starch-coated linerboard to a constant moisture gradient and determining the metal content change near the noncoated surface. We understand that real-life humidity conditions generally are cyclic and therefore may involve metal movement due to the possible repetitious moisture condensation that may occur within the paperboard. However, this study was designed to determine whether migration occurs under constant conditions.

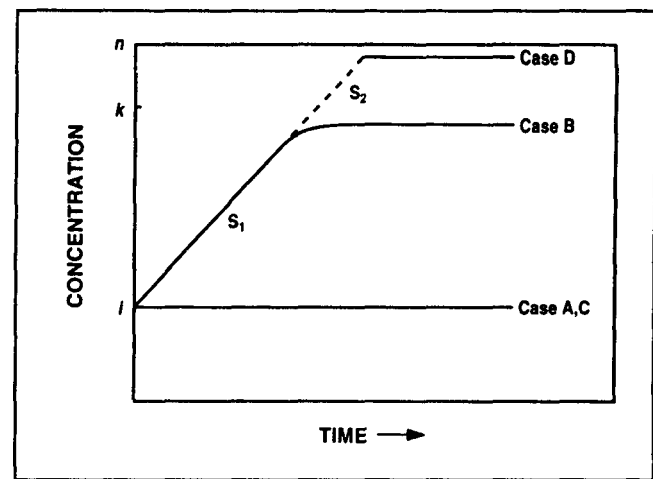
BACKGROUND

CORRUGATED FIBERBOARD

For products to be impregnated by metals from the starch adhesive used to bind the component paperboards (Fig. 1), the metals must migrate from the singleface glue line through the singleface linerboard to its outer surface, the side that normally faces to the inside of the container. A similar migration to the surface of the doubleback linerboard, i.e., to the outside of the box, would not result in metallic impregnation of the contents. A probable cause of metal migration could be a hydrodynamic driving force caused by a difference in humidity on the outside as opposed to inside surfaces of the box. Although many possible moisture gradients may occur in real life, this study dealt only with the situation in



1. Structure of corrugated fiberboard with metals in glueline



2. Metal concentration in outer layer of linerboard as a function of time

which the temperature is equal on both surfaces and there is high humidity on the outside (doubleback) surface and low humidity on the inside (singleface) surface. Under these conditions, a constant moisture gradient exists, and the moisture flow rate through the specimens should be constant.

The metals in the starch may migrate only from the singleface glueline (Fig. 1, L)—that portion of the singleface linerboard lying between flute tips should not be a source of wash-water metals. For the doubleback glueline to be a metal source, the metals must migrate from the doubleback glueline inwardly along the medium to the singleface glueline. Thus, for any metals possibly introduced to the starch from flexographic wash water, it is the singleface glueline that would be expected to be the primary transference site between the container and its contents.

Migration behavior at the glueline

The metals, if weakly bonded orionic, should be free to migrate from the starch into the paperboard. Only then should they pass through the linerboard to its outer surface and concentrate there. Several scenarios are possible.

Near the outer surface of the linerboard, the metal concentration/time

behavior follows one of four possible cases (Fig. 2):

A. Metals are fixed in both the paper and starch. The concentration remains constant at the initial paperboard concentration (i).

B. Metals are fixed in the starch and free to migrate in the paper. Metals in the paperboard could migrate and concentrate in layer C (Fig. 3) at a higher concentration (k) than the initial level (i). Metals in the starch remain in the starch.

C. Metals are fixed in the paper but could be free to migrate from the starch. The starch metals become fixed at the interface. The analyzed layer C of the paperboard would be identical with that in Case A.

D. Metals could be free to migrate in both the paperboard and starch. Metals in the paper could migrate to the analyzed layer C at the same rate and level as that for Case B, followed by the metals from the starch. The graph would have two parts, corresponding to the paperboard metals, up to level k , and the starch metals, to a level n above k . The two slopes maybe different. Only Case D allows for the migration of wash-water metals to the container/product interface.

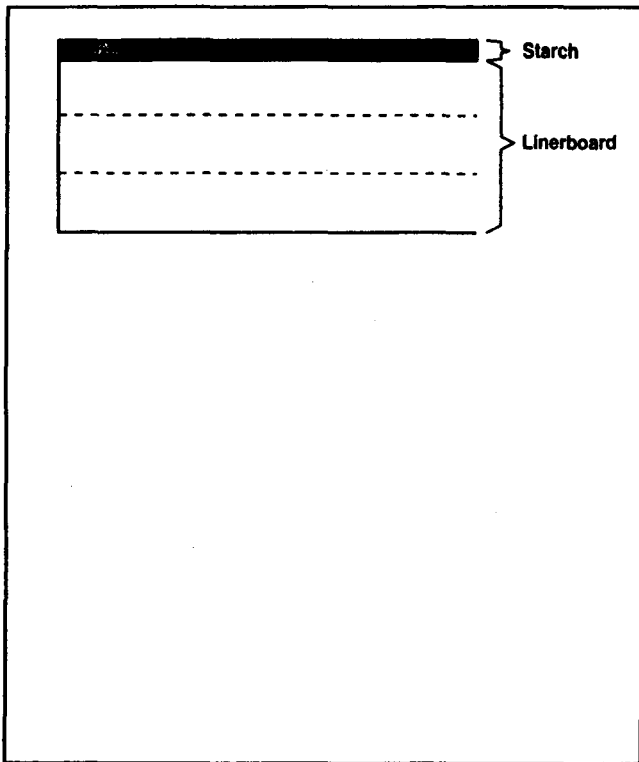
Two other scenarios maybe possible (but are left to future study):

E. The metals could migrate by diffusion as a result of the concentration gradient of the metals themselves within the sheet. As the metals migrate toward layer C as a result of the moisture gradient, their increased concentration would cause them to counter-diffuse back into the sheet; apparent migration rates would be summation rates, indicating the predominating driving force.

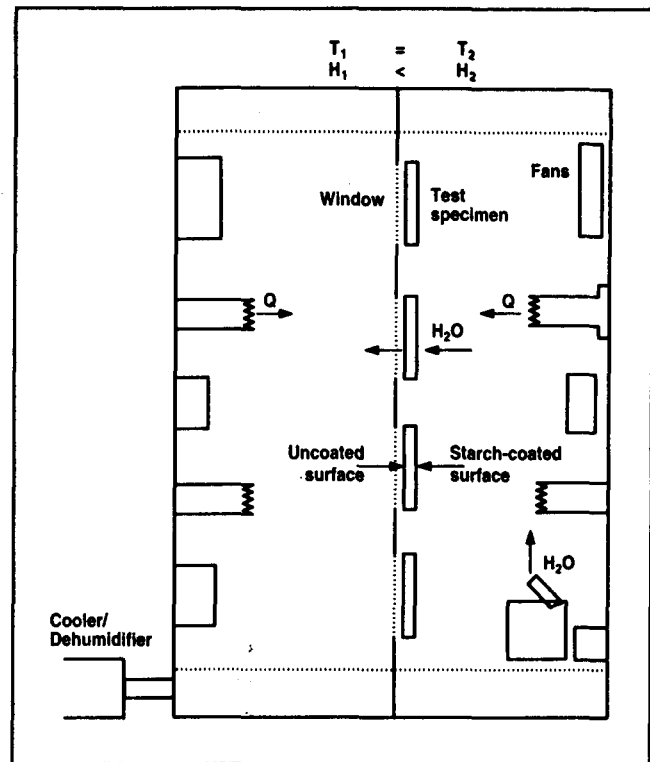
F. Vapor-phase migration could exist. Some metals, such as mercury, have high vapor pressures and may migrate in the air stream as the air and moisture vapor move through the sheet. This mechanism would depend on the particular chemical compound for the metal and its bonded state within the paperboard.

Metal levels in adhesive

Metal migration rates may depend on the concentration of metals in the water used to prepare the starch. Testing for the concentration effect requires concurrent exposure of samples having either a low or high level of metal in the starch. Since the flexographic wash water is presumed to have a high level of metals, fresh tap water can be presumed to be a low-level source of metal. We tested the effect of metal concentration by evaluating two sets of samples: one



3. Cross-sectional view of linerboard with starch coating. Zone A is adjacent to starch, zone B in the middle of sheet, and zone C in the outer layer of the sheet.



4. Schematic of exposure chamber for concurrent testing of 20 specimens. Temp. = 23°C; $H_1 = 30\%$ RH; $H_2 = 80\%$ RH.

made with starch prepared with flexographic wash water and the other with starch prepared with tap water.

Flexographic wash water is known to cause premature starch viscosity breakdown. This problem can be corrected by including a starch viscosity stabilizer with the flexographic wash water, but the addition of a stabilizer may affect the rate of metal migration. We tested for this effect by including a set of samples that contained a viscosity stabilizer in the starch made with flexographic wash water. If the stabilizer fixed the metals in the starch, the samples would respond like a Case A scenario instead of Case C, or a Case B scenario instead of Case D.

EXPERIMENTAL

Simulated glueline exposure

We expected the flexographic wash-water metal concentrations to be relatively low and yet significantly higher than the metal concentrations

in fresh tap water (based on a discussion with an ink producer). Consequently, a large area of glueline was required for analysis. Therefore, rather than exposing corrugated board to the moisture gradient, we used a simulated glueline. A sheet of linerboard was coated on one surface with corrugating starch adhesive and gelled. Three batches of starch were prepared using (a) fresh water; (b) flexographic wash water obtained from a boxmaker's printing plant during a typical cleanup operation (for all solutions except sodium hydroxide preparations; metallic hydroxides might precipitate out and not be included in the starch); and (c) the same formula as (b) but including HARLOFLEX, a chemical viscosity stabilizer.*

The three types of coated sheets, each simulating a glueline several centimeters wide, were mounted in frames

* The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

and placed in a dual-zoned humidity chamber (Fig. 4) maintained at 23°C. An 80%-RH environment was in contact with the starched surface and a 30%-RH environment was in contact with the uncoated surface of the linerboard. Moisture was thus free to migrate through the starch layer and then through the linerboard. The water transmission rate was 2.44 L/m²/day through the samples. Temperature and humidity were controlled using two Honeywell DR4500 controlling recorders, one for each zone.

Paperboard samples

Commercial 205-g/m² unbleached kraft linerboard was cut into 240 x 300 mm sheets, coated with the appropriate starch, and sandwiched between two plastic frames using contact cement. The plastic frames gave a flat, tight seal when mounted in the chamber and prevented moisture from moving through the frames rather than the linerboard. Twenty specimens were mounted and exposed concurrently. Specimens of

I. Metal contents of unexposed test specimens

Sample	Metal concentration (ppm)*										
	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Se	Zn
Paper as supplied (average)	11.9	0.43	0.37	0.53	2.9	21.7	1.24	1.44	4.11	12.7	9.2
Corrugating starch	14.2	0.17	0.61	0.50	2.6	19.4	0.84	1.23	3.89	13.4	10.9
Household starch	13.0	0.30	0.49	0.52	2.7	20.5	1.04	1.33	4.00	13.0	10.0
	<2.8	<0.1	<0.2	<0.2	<0.3	<.04	<0.2	<0.4	<1.1	<1.9	<0.2
	<2.8	<0.1	<0.2	<0.2	<0.3	0.03	<0.2	0.4	<1.1	<1.9	<0.1

*Analyzed at University of Wisconsin Soil and Plant Analysis Laboratory using inductively-coupled plasma emission spectroscopy (14)

II. Metal contents of paperboard samples before exposure^a

Metal	Paperboard with starch layer removed ^b						Paperboard with starch layer intact ^c					
	Fresh water		Wash water		Wash water with chemical		Fresh water		Wash water		Wash water with chemical	
	Avg., ppm	COV, %	Avg., ppm	COV, %	Avg., ppm	COV, %	Avg., ppm	COV, %	Avg., ppm	COV, %	Avg., ppm	COV, %
	As	10.7	34	16.8	25	10.8	53	5.0	24	8.2	18	9.5
Cd	0.34	54	0.38	21	0.32	51	0.19	60	0.21	51	0.23	38
Co	1.07	68	1.24	62	0.84	30	0.49	56	0.83	75	0.89	64
Cr	0.95	57	1.68	108	0.82	36	0.74	17	0.81	11	1.72	101
Cu	6.0	19	4.4	27	5.0	30	14.6	18	14.2	36	14.2	57
Mn	15.5	38	20.0	16	12.5	73	13.4	7	17.1	5	16.6	18
Mo	1.17	24	1.52	40	1.32	26	1.00	8	1.24	26	1.33	51
Ni	1.60	18	1.52	25	1.79	17	0.87	22	1.13	43	1.80	97
Pb	3.54	35	5.44	15	3.34	66	2.36	15	2.76	19	3.00	40
Se	11.1	35	17.6	20	19.0	59	4.8	11	8.8	27	9.6	50
Zn	13.8	36	14.1	15	11.7	18	20.6	42	16.4	11	21.9	19

^aStarch slurry prepared using fresh water, wash water, or wash water plus chemical viscosity stabilizer. Avg. = average of four (or five) individual samples analyzed; COV = coefficient of variation, equal to standard deviation divided by average, times 100.
^bStarch layer and layers A and B removed from paperboard (Fig. 3). Paperboard layer C analyzed for metals.
^cLayers B and C removed from paperboard (Fig. 3). Starch layer and layer A analyzed for metals.

the “blanks” (fresh water in adhesive), “wash water,” and “wash water with chemical” (the viscosity stabilizer HARLOFLEX) were randomly positioned in the chamber, removed after various exposure times, and analyzed. New sheets were continually placed in the chamber as specimens were removed. Replicated data were obtained from specimens exposed at various times; e.g., all of the eight-week samples were installed and removed at different times during the course of the study.

A total of 23 specimens of each type of coated board (69 specimens total) were analyzed; exposure times

ranged from 2 weeks to 12 weeks.

Adhesive preparation and application

The adhesive was a carrier-type, unmodified starch formula with 20-21% solids; it was applied to the liners-boards using the Forest Products Laboratory glue machine normally used for doublebacking. The glue gap was 0.23 mm. The volume of starch applied was assumed to be constant for all sheets. The adhesive was gelled using a photodryer-type heating unit. Restraint provided by the wire kept the sheet flat.

Specimen preparation for analysis

Paperboard samples were removed from the chamber after a suitable exposure time, removed from the frames using a razor knife, and surface-ground to remove the starch layer and two thirds of the paperboard thickness (Fig. 3, layers A and B). Grinding the sheets has the potential of adding grinder wheel dust to the sample and of driving starch residue into the remaining portion of paperboard (Fig. 3, layer C). To minimize the latter possibility, the grinding wheel was cleaned and refaced with a diamond-tipped tool after removing the starch and layer A

III. Linear regression data for metal concentrations as a function of time

Metal	Starch water	Slope, ppm/week	Intercept conc., ppm	Coefficient of determination
As	FW	0.4333	8.424	0.1080
	WW	0.0747	12.668	0.0052
	WWC	0.5327	6.336	0.1479
Cd	FW	0.00409	0.259	0.0149
	WW	-0.00053	0.287	0.0002
	WWC	0.00644	0.216	0.0320
Co	FW	-0.1404	2.236	0.2325
	WW	-0.1880	2.463	0.3862
	WWC	-0.1757	2.468	0.2197
Cr	FW	0.05131	0.636	0.0349
	WW	0.01323	0.796	0.0026
	WWC	0.04463	0.553	0.0363
Cu	FW	0.1655	5.636	0.0425
	WW	-0.1511	6.442	0.1040
	WWC	-0.079	5.104	0.0463
Mn	FW	0.9408	12.98	0.3492
	WW	0.3327	17.76	0.1662
	WWC	0.8997	13.24	0.2682
Mo	FW	0.03544	0.670	0.1481
	WW	0.00431	0.993	0.0022
	WWC	0.04033	0.569	0.1350
Ni	FW	0.01457	1.132	0.0171
	WW	0.00434	1.181	0.0023
	WWC	-0.0122	1.297	0.0114
Pb	FW	0.1940	2.976	0.1929
	WW	0.0999	4.242	0.0486
	WWC	0.2459	2.131	0.1864
Se	FW	0.4051	9.403	0.0946
	WW	0.0571	13.611	0.0026
	WWC	0.5254	7.235	0.1326
Zn	FW	0.3911	12.04	0.0706
	WW	0.2081	13.49	0.0120
	WWC	0.0411	12.87	0.0046

of the paperboard. A vacuum near the wheel removed grinder dust as it was generated, thereby minimizing contamination.

Any residual dust was carefully removed to reduce the possibility of its reintroduction to the specimen in the next grinding pass. A second pass of the grinding wheel removed layer B and should have removed any starch that had been driven into the sheet during the first pass. The final thickness of layer C was approximately 0.10 mm. This layer then was subjected to inductively coupled plasma emission spectroscopy (14).

RESULTS AND DISCUSSION

Initial metal concentrations

The metal concentrations of the paperboard and corrugating starch used in this study are given in Tables I and II. The metal concentrations of the corrugating starch can be considered negligible because they were of the same concentrations as that of a food-grade (household) starch, which was very low compared to the metal concentration of the paperboard itself.

The paperboard had only trace amounts of cadmium, chromium,

cobalt, and molybdenum, all about 1 ppm or less (Table II). The amounts of copper, lead, and nickel were slightly higher but still less than 5 ppm. The paperboard appeared to have higher concentrations of arsenic, manganese, selenium, and zinc.

Effect of grinding

Removal of the starch layer and the adjacent two layers of the coated paperboard left a layer consisting of only paperboard, which should have had the same metal concentrations as that of the supplied paperboard. The data showed no significant difference in metal content for samples ground in this manner compared to uncoated paperboard at the two-sigma confidence levels tested (>95%) (Table II). However, a high coefficient of variation resulted from analysis of four or five specimens of each type of coated sheet. Metal concentrations for all three types of coated board within this "ground-down" set showed a similarly high degree of scatter, thereby eliminating any interpretation of differences between the three types of adhesive preparations. Whether the excessive variability was a consequence of the grinding process or reflects the limits of the metal analysis is not known.

Reversing the grinding process—removing layers B and C, leaving the starch layer and paper layer A—resulted in metal concentrations indicative of the metal in the starch (Table II). Because the specimen analyzed was partly paperboard and partly metal-free starch, the metal concentrations were expected to be less than the concentrations of the paperboard alone. This was the case for arsenic, cadmium, cobalt, lead, and selenium, and nearly so for chromium, nickel, and manganese. Copper and zinc showed a strong increase in concentration. Both of these metals are present in standard copper piping applications; thus, their increase was not totally unexpected. The problem with this argument is

that the quantities of these metals were of the same magnitude whether fresh water or flexographic wash water was used for the starch preparation. The starch may have been contaminated by the photodryer screen during gelling. We did not expect the apparent lack of an increase in metals (other than copper and zinc). This result would seem to imply the absence of such metals in the wash water. Apparently any metals introduced to the starch via the wash water were masked by the background metal concentrations in the paperboard.

Effect of exposure time

A high level of scatter was again observed. Under a constant driving force, metals would move at a constant rate to layer C of the paperboard, and the concentration there should increase linearly with time. To determine whether migration had taken place, a linear regression of the data was made using the least-squares method. The resulting slopes, intercepts, and coefficients of determination (R^2 values) are given in **Table III**. In all cases, the slopes were very small, intercept values were relatively close to the initial concentrations (Table II, paperboard without starch), and coefficients of determination were very low there is a very low probability that changes in concentration occurred in paperboard layer C, even after 12 weeks of exposure.

Table IV shows the average metal concentrations for the 23 exposed samples. As the data indicate, most of these average values are close to the initial concentrations (Table II); with one exception, all are within two sigma units of the initial concentration, implying a >95% probability that the average values are not different from the initial concentrations. Only the 1.68-ppm initial concentration for chromium wash water lies beyond the two-sigma limit, implying that there is a >95% probability that this value is simply an outlier. The

IV. Metal concentrations after exposure to moisture gradient *

Metal	Starch water	Avg. conc., ppm	Standard deviation, ppm	Coefficient of variation, %
As	FW	11.3	4.3	38
	WW	13.0	3.4	26
	WWC	9.8	4.5	46
Cd	FW	0.27	0.10	35
	WW	0.26	0.09	35
	WWC	0.24	0.09	38
Co	FW	1.31	0.95	72
	WW	1.10	0.86	79
	WWC	1.05	0.86	83
Cr	FW	0.75	0.47	63
	WW	0.61	0.36	58
	WWC	0.65	0.40	61
Cu	FW	6.53	2.40	37
	WW	5.41	1.53	28
	WWC	4.36	1.22	27
Mn	FW	20.0	3.9	19
	WW	20.3	2.4	12
	WWC	20.2	4.4	21
Mo	FW	0.96	0.20	21
	WW	1.02	0.30	30
	WWC	0.82	0.34	42
Ni	FW	1.21	0.35	29
	WW	1.20	0.29	24
	WWC	1.19	0.35	29
Pb	FW	4.45	1.27	28
	WW	4.88	1.50	31
	WWC	3.79	1.85	49
Se	FW	12.6	3.5	28
	WW	14.2	3.1	22
	WWC	10.6	5.0	47
Zn	FW	13.6	2.5	18
	WW	13.5	3.8	28
	WWC	13.2	2.0	15

*Specimens analyzed at University of Wisconsin Soil and Plant Analysis Laboratory using inductively-coupled plasma emission spectroscopy (14)

data imply that case A or C is operating.

Additional work is needed to increase the confidence level of these findings. In addition, at least two environmental variables could be examined: cyclic humidity and low temperatures. Cyclic humidity reflects the diurnal conditions of day/night fluctuations in humidity, and low temperatures are typical of refrigerator/freezer storage. Also, the apparently low level of metals in the commercially obtained flexographic wash water precludes any definite statement on the actual migration from the starch where the metals were present. Additional studies are

needed to explore the situation in which the water used in the starch preparation contains considerably higher metal concentrations than does the paperboard.

CONCLUSIONS

Our research lead us to the following conclusions:

1. Paperboard itself may be a larger source of metals than is the flexographic wash water. Metal concentrations in the starch adhesives prepared with flexographic wash water and with fresh water were very low and were indiscernible from the background metal contained in the

paperboard. A survey would be needed to establish the range of metal concentrations that exist for flexographic wash water and for various linerboards.

2. Metals apparently did not migrate within the linerboard. Time/ exposure tests using constant relative humidities of 80% and 30% at 23°C showed nonsignificant change in metal concentrations after a 12-week exposure period.
3. We do not know if metals migrate from starch to linerboard. The apparent low levels of metal in the commercially supplied wash water, together with the low or nonexistent metal migration rates observed for the linerboard, preclude determining whether metals migrated from starch to linerboard.

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