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UTILIZATION OF CALCITE PRODUCED IN TURKEY FOR PAPER COATING

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ABSTRACT

Calcium carbonate is one of the coating pigments widely used in paper industry. Especially, in recent years calcium carbonate filler has gained high importance in alkaline pulping. In Turkey industry actually imports calcium carbonate; whereas, there are rich calcite reservoirs in the country. In this study two different types of domestic ground (GCC) calcite samples were used. Physical and chemical properties of calcite samples were tested firstly. $CaCO_3$ percentages of both samples were 97.3 % and 97.6 % (min. 95 % $CaCO_3$). $MgCO_3$ and Fe_2O_3 percentages were within the desired limits. Brightness values were 95.5 % and 94.5 % and yellowness 1.1 % and 1.5 % elrepho. These values also were within the requested limits. Under 2 microns particle size and over 10 microns particle size fractions were 95 % and 89 % (min. 80) and 1 % and 2 % (max. 2) respectively. Dry matter rates were between 40 %-65 %, for the pilot plant-coating machine. During the preparation of coating color calcium carbonate has been used together with kaolin. The ratios of calcium carbonate to kaolin were 30/70, 40/60, 50/50, 60/40, 70/30, 100/0. In coating color preparation latex was used as a binder because of its wide applications. Latex percentages were 11, 12, and 13 %. Coated papers were glossed and physically tested. As a result, both calcium carbonate samples were found suitable for using in coating color preparation. By the utilization of domestic calcium carbonate in coated paper production, there will be foreign currencies saving.

Key Words : Calcite, Paper coating, Pigments, Gloss, Yellowness

TÜRKİYE'DE ÜRETİLEN KALSİTİN KUŞE KAĞIT YAPIMINDA KULLANILMASI

ÖZET

Kalsit ($CaCO_3$), kağıt endüstrisinde yaygın olarak kullanılan bir kuşeleme pigmentidir. Ayrıca, son yıllarda kalsit, dolgu maddesi olarak uzun ömürlü alkali kağıt yapımında da büyük bir önem kazanmıştır. Türkiye'de zengin kalsit yatakları olmasına rağmen kağıt sanayiinde kullanılan kalsit ithal edilmektedir. Bu çalışmada, iki tip yerli toz (GCC) kalsit kullanılmıştır. Bu örneklerin $CaCO_3$ oranı % 97.3 ve % 97.6 (min. % 95)'dır. $MgCO_3$ ve Fe_2O_3 oranları ise, istenen sınırlar içersindedir. Örneğin parlaklık değerleri % 95.5 ve % 94.5 sarılık değerleri ise % 1.1 ve % 1.5 elrepho olarak belirlenmiştir. 2 mikronun altındaki ve 10 mikronun üzerindeki fraksiyonlar sırasıyla % 95, % 89 ve %1 ve % 2 olarak bulunmuştur. Kuşe pilot tesisinde, kuşe boyası konsantrasyonu % 40- % 65 arasında alınmıştır. Hazırlanan kuşe boyasının kalsit ve kaolen oranları 30/70, 40/60, 50/50, 60/40, 70/30 ve 100/0'dır. Kullanılan latex yapıştırıcı değerleri ise % 11, % 12 ve % 13'dür. Kuşelenen kağıtlar perdahlama öncesi ve sonrası fiziksel ve optik testlere tabi tutulmuşlardır. Sonuç olarak her iki $CaCO_3$ örneklerinin fiziksel ve optik özellikleri bakımından kuşeleme için uygun olduğu anlaşılmıştır. Yerli kalsit rezervlerinin kullanılması ülkemiz için döviz tasarrufu sağlayacaktır.

Anahtar Kelimeler : Kalsit, Kuşeleme, Pigment, Perdah, Sarılık

1. INTRODUCTION

Coating is the application of different coating formulation on base paper surface whereas pigment coating is the application of pigment adhesive mixture on the paper surface. Base paper used for coating should be less porous and have a good formation with evenly fiber distribution. On the other hand, pigment used should give smooth surface, homogenous ink penetration and high brightness to the coated paper. In order to utilize from the properties of two different pigments, pigment mixture has been used. For example, kaolin-calcite mixture has been used to benefit smooth surface giving ability of kaolin and high brightness of calcite. Most widely used pigments are kaolin, calcium carbonate, titanium dioxide, zinc sulfite, satin white and colored pigments. Coating imparts to the paper smooth surface, high printing quality and high brightness and contrast property between black ink and white paper (Jaussaud and Vallette, 1974; Eroğlu, 1990).

One of the most important properties of a pigment is its adhesive demand. Namely, the glue quality required in order not to form dust or not to occur separation from paper surface. Lower adhesive demand is a desired property. This quantity varies with particle size. Generally, starch, casein, soybean, polyvinyl alcohol and synthetic latex have been used as adhesives.

When coating is done on paper machine during papermaking, it is called on machine coating. But generally, high quality coated papers are made on separate coating machines. Coating on separate coating machines is more expensive but it is a much more practical despite its higher cost (Casey, 1961).

In Turkey, calcite used for paper coating has been imported. Whereas, there are rich calcite reservoirs in Turkey not only for indigenous use but also for exporting. However, it should be kept in mind that calcite produced should meet specifications needed for coating. In Turkey, 145.000 tons/year coated paper and 165.000 tons/year coated paperboard have been produced. Consequently, the cost of coated paper is 20 % higher compared with European countries (Koç, 2000).

The aim of this study was to determine suitability of indigenous calcite for paper coating. For this purpose two samples of calcite provided from two calcite producer firms (Erciyes and Hisersan) in Turkey. Physical and chemical properties of calcite sample 1 and calcite sample 2 were determined and different coating formulations were prepared conform to the standard specifications. After coating and machine glossing, physical and optical properties of coated papers were determined.

2. MATERIAL AND METHOD

In Turkey, high brightness and high purity calcite have been produced in Niğde, Muğla and Çanakkale province. Two calcite samples used in this study were taken from Niğde province.

Approximate chemical composition of samples were 55.6 % CaO, 40 % MgO, 0.5 % FeO, 0.5 % Al_2O_3, 0 % SiO_2. Physical and chemical tests such as base paper humidity, sample humidity, insoluble in acid, $CaCO_3$ %, $MgCO_3$ %, Fe_2O_3 %,abrasive test, particle size, viscosity, brightness, pH, Denisson wax test, Cobb test, breaking length, smoothness, IGT printing test and thickness have been done to determine suitability of calcite samples for coating.

For the preparation of coating color 11 %, 12 % and 13 % latex was used as adhesive on the basis of pigments weight. Calcite , kaolin mixture ratios were 30-70 %, 40-60 %, 50-50 %, 60-40 %, 70-30 %, 100-0 % respectively. On the other hand, 0.3 % brightener and 0.0005 indigo blue were used. Dry matter rate, viscosity and pH values were 63 %, 500-600 cp and 8.5-9.2 respectively.

To coat base papers Dixon coater existing at SEKA Dalaman mill was used. One surface of the sample papers were coated. After coating; basis weight, moisture, ash contents of the papers were determined. After conditioning brightness, yellowness, Denisson wax number, Cobb test and tensile strength tests were realized. In addition, after machine glossing, brightness, yellowness, gloss, IGT and thickness values were determined. TAPPI standard test methods were used for all tests performed.

3. RESULTS

3. 1. Physical and Chemical Tests

Sample I, sample II and SEKA Dalaman coating and filler calcite physical and chemical properties are given Table 1.

As can be observed from Table 1 sample 1 coating calcite has an 89 % fraction of less than 2 micron and 2 % fraction of more than 10 micron. Brightness being 94.5 % and yellowness 1.5 %. The samples have low abrasion values.

Table 1. Physical and Chemical Properties of SEKA Dalaman Coating and Filler $CaCO_3$ and Calcite Samples Used

Properties			Coating $CaCO_3$	Filler $CaCO_3$	Sample 1 $CaCO_3$	Sample 2 $CaCO_3$
Chemical Properties	$CaCO_3$ (%)		95 min.	95 min.	97.6	97.3
	$MgCO_3$ (%)		2 max.	2 max.	1.3	1.3
	Fe_2O_3 (%)		0.5 max.	0.5 max.	-	-
	Insoluble in acid (%)		0.5 max.	0.5 max.	0.41	0.48
Physical Properties	Humidity (%)		1 max.	-	0.4	29.1
	Brightness (Elrepho R 457, %)		92 min.	95 min.	94.5	95.5
	Yellowness (Elrepho, %)		4 max.	4 max.	1.5	1.1
	Viscosity (cp, 70 % dry matter brookfield 60 rpm)		700 max.	-	55 (% 10 ispersant min.)	188 (predisperse min.)
	Particle size	Under 2 μm (%)	80 min.	42 min.	89	95
		Over 10 μm (%)	2 max.	5 max.	2	1
		Over 45 μm (%)	-	-	-	-
	Abrasion value (mg).		25 max.	25 max.	14	17

On the other hand, sample 2 has as high as 95 % fraction of particle size less than 2 micron. The fraction having more than 10 micron particle size was 1 %. This sample has the highest brightness of 95.5 % and lower yellowness than other samples with 1.1 % yellowness. Abrasiveness was found to be as 17 mg. It has been concluded that both samples are suitable pigments for coating applications.

Physical and optical properties of base paper used for coating experiments are given in Table 2.

Table 2. Physical and Optical Properties of Base Paper Used

Properties	Values
Grammage (g/m^2)	66 (66.2-67.3)
Humidity (%)	4.7
Cobb (g/m^2, 1 min.)	Screen = 25.9, Felt = 26.8
Brightness (Elrepho R – 457, %)	88.6
Yellowness (Elrepho R – 457, %)	-5.3
Breaking length (m)	Length X width = 5500 x 2900
Denisson number	16-18-20
Ash content (%)	11.0

3. 2. Tests Performed Before Machine Glossing

Before machine glossing, physical and optical properties of both samples were determined. The properties were determined after 3-6 hours conditioning at temperature of 20 ± 2 °C and relative humidity of 65 ± 5 %. Physical and optical properties of paper coated with sample 1 calcite by using 11 % latex at 50-60 % dry matter rate are given in Table 3. Physical and optical properties of paper coated with sample 1 calcite, by using 12 % and 13 % latex as adhesive are given in Table 4 and Table 5 respectively.

Table 3. Physical and Optical Properties of Paper Coated With Sample 1 Calcite, by Using 11% Latex as Adhesive

Calcite ratio (%)	30	40	50	60	70	100
Grammage (g/m^2)	77.6	78.2	77.8	77.9	78.0	78.4
Humidity (%)	5.4	5.9	5.9	5.2	5.9	5.8
Ash content (%)	17.8	18.2	17.9	18.4	19.0	19.8
Brightness (Elrepho R-457, %)	87.4	87.9	88.0	88.2	88.7	89.2
Yellowness (Elrepho R-457, %)	-1.4	-1.5	-1.76	-1.8	-2.2	-2.8
Dennisson number	3-4-5	3-4-5	3-4-5	3-4-5	4-5-6	5-6-7
Cobb (g/m^2, 1 min.)	31.5	32.8	31.5	30.1	32.0	32.1
Breaking length (m)	5316	5299	5316	5351	5385	5385

Table 4. Physical and Optical Properties of Paper Coated With Sample 1 Calcite, By Using 12 % Latex at 40-60 % Dry Matter

Calcite ratio (%)	30	40	50	60	70	100
Grammage (g/m^2)	78.7	79.0	78.5	78.4	77.7	77.9
Humidity (%)	6.3	5.4	6.5	5.7	6.2	6.3
Ash content (%)	18.2	18.3	18.1	18.0	18.5	18.8
Brightness (Elrepho R-457, %)	87.3	87.5	87.8	88.1	88.4	89.0
Yellowness (Elrepho R-457, %)	-1.2	-1.3	-1.6	-1.7	-2.0	-2.5
Dennisson number	4-5-6	4-5-6	4-5-6	5-6-7	6-7-8	5-6-7
Cobb (g/m^2, 1 min.)	28.7	28.0	27.8	27.3	28.0	27.8
Breaking length (m)	5485	5167	5316	5232	4957	5214

Table 5. Physical and Optical Properties of Paper Coated with Sample 1 Calcite, by Using 13% Latex at 55-65 Dry Matter

Calcite ratio (%)	30	40	50	60	70	100
Grammage (g/m^2)	78.1	78.5	78.0	77.7	77.6	78.3
Humidity (%)	5.4	5.7	5.7	5.6	5.7	5.8
Ash content (%)	18.5	18.8	18.2	18.3	19.0	19.7
Brightness (Elrepho R-457, %)	87.2	87.4	87.6	87.9	88.0	88.8
Yellowness (Elrepho R-457, %)	-1.0	-1.1	-1.3	-1.5	-1.7	-2.3
Dennisson number	4-5-6	5-6-7	5-6-7	5-6-7	5-6-7	5-6-7
Cobb (g/m^2, 1 min.)	27.6	27.0	27.0	26.7	27.2	27.6
Breaking length (m)	4957	5148	5128	4957	5108	4957

On the other hand, physical and optical properties of paper coated with sample 2 calcite by using 11 %, 12 % and 13 % latex as adhesive are given Table 6, Table 7 and Table 8 respectively.

Table 6. Physical and Optical Properties of Paper Coated With Sample 2 Calcite, by Using 11 % Latex at 50-65 % Dry Matter.

Calcite ratio (%)	30	40	50	60	70	100
Grammage (g/m^2)	78.0	77.8	78.3	77.3	77.2	78.8
Humidity (%)	4.7	5.7	5.4	5.2	5.2	5.4
Ash content (%)	19.1	19.3	20.0	18.5	17.8	20.6
Brightness (Elrepho R-457, %)	87.5	87.6	87.9	88.1	88.8	89.4
Yellowness (Elrepho R-457, %)	-1.5	-1.6	-1.7	-1.9	-2.3	-3.0
Dennisson number	3-4-5	4-5-6	4-5-6	4-5-6	4-5-6	4-5-6
Cobb (g/m^2, 1 min.)	29.6	27.0	26.5	26.0	26.2	26.0
Breaking length (m)	6162	6869	6263	6768	6566	6263

Table 7. Physical and Optical Properties of Paper Coated with Sample 2 Calcite, By Using 12% Latex At 40-60 % Dry Matter

Calcite ratio (%)	30	40	50	60	70	100
Grammage (g/m^2)	78.7	78.2	78.3	77.7	77.5	77.0
Humidity (%)	4.4	4.6	5.0	4.7	4.8	4.7
Ash content (%)	20.1	20.0	19.1	19.3	19.6	19.1
Brightness (Elrepho R-457, %)	87.4	87.5	87.7	88.0	88.5	89.0
Yellowness (Elrepho R-457, %)	-1.3	-1.5	-1.6	-1.8	-2.2	-2.7
Dennisson number	4-5-6	4-5-6	4-5-6	4-5-6	5-6-7	5-6-7
Cobb (g/m^2, 1 min.)	29.5	26.8	26.0	26.0	26.5	28.0
Breaking length (m)	6667	6566	6465	6768	7071	6965

Table 8. Physical and Optical Properties of Paper Coated with Sample 2 Calcite, by Using 13 % Latex at 55-60 % Dry Matter

Calcite ratio (%)	30	40	50	60	70	100
Grammage (g/m^2)	78.0	78.7	78.1	78.0	77.7	78.3
Humidity (%)	4.3	4.7	4.6	4.4	4.5	4.4
Ash content (%)	19.1	20.1	19.8	19.3	18.5	19.5
Brightness (Elrepho R-457, %)	87.1	87.2	87.6	87.7	88.1	88.8
Yellowness (Elrepho R-457, %)	-1.2	-1.4	-1.5	-1.6	-1.9	-2.4
Dennisson number	5-6-7	5-6-7	5-6-7	5-6-7	5-6-7	6-7
Cobb (g/m^2, 1 min.)	26.6	27.7	27.5	26.5	27.0	27.0
Breaking length (m)	6263	6667	6965	6667	6768	6566

3. 3. Tests Performed After Machine Glossing

For gloss determination 50-60 measures were performed. Mean value of mostly repeated 10 values was considered as average gloss. The reasons for these are sensitivity of gloss apparatus and gloss value variation of different closer points on the paper. Physical and optical properties of glossed papers coated with sample 1 calcite by using 11 %, 12 %, 13 % latex are given in Table 9, Table 10, Table 11 respectively.

Table 9. Physical and Optical Properties of Glossed Sample 1 Calcite Coated Papers by Using 11 % Latex

Calcite ratio (%)	30	40	50	60	70	100
Humidity (%)	5.3	4.6	5.0	5.0	4.8	5.0
Brightness (Elrepho R-457, %)	86.3	86.5	86.6	86.8	87.1	87.8
Yellowness (Elrepho R-457, %)	-1.5	-1.6	-1.9	-2.3	-3.0	-3.5
Gloss (fotovolt 75°C)	74.0	72.0	69.0	68.2	67.0	57.5
IGT (cm/sn)	> 116	>116	>116	>116	>116	>116
Thickness (mm)	0.065	0.065	0.065	0.065	0.065	0.065

Table 10. Physical and Optical Properties of Glossed Sample 1 Calcite Coated Papers by Using 12% Latex.

Calcite ratio (%)	30	40	50	60	70	100
Humidity (%)	4.6	4.9	4.7	5.0	4.8	5.2
Brightness (Elrepho R-457, %)	85.7	85.9	86.3	86.7	87.0	87.6
Yellowness (Elrepho R-457, %)	-1.4	-1.5	-1.7	-2.1	-2.6	-3.2
Gloss (fotovolt 75°C)	78.0	75.0	72.0	69.0	68.0	58.5
IGT (cm/sn)	>116	>116	>116	>116	>116	>116
Thickness (mm)	0.065	0.065	0.065	0.065	0.065	0.065

Table 11. Physical and Optical Properties of Glossed Sample 1 Calcite Coated Papers by Using 13% Latex.

Calcite ratio (%)	30	40	50	60	70	100
Humidity (%)	4.8	5.1	5.2	5.2	5.2	5.4
Brightness (Elrepho R-457, %)	85.6	85.8	86.2	86.6	86.9	87.5
Yellowness (Elrepho R-457, %)	-1.3	-1.4	-1.5	-1.6	-2.0	-2.7
Gloss (fotovolt 75°C)	82.6	78.0	74.5	71.6	69.0	63.0
IGT (cm/sn)	>116	>116	>116	>116	>116	>116
Thickness (mm)	0.065	0.065	0.065	0.065	0.065	0.065

When comparing Table 3, 4 and 5 with Table 9, 10 and 11 it can be easily seen that yellowness values are decreased with the decrease of glossing of sample 1. Whereas, brightness is slightly increased with the decrease of glossing of sample 1.

On the other hand, physical and optical properties of glossed papers coated with sample 2 calcite by using 11 %, 12 % and 13 % latex are given Table 12, Table 13 and Table 14 respectively.

Table 12.Physical and Optical Properties of Glossed Sample 2 Calcite Coated Papers by Using 11% Latex.

Calcite ratio (%)	30	40	50	60	70	100
Humidity (%)	5.1	5.2	4.9	5.0	4.7	5.3
Brightness (Elrepho R-457, %)	86.5	86.7	86.8	87.0	87.4	88.0
Yellowness (Elrepho R-457, %)	-1.6	-1.7	-1.9	-2.4	-3.1	-3.6
Gloss (fotovolt 75°C)	80.8	78.7	74.0	69.0	66.5	60.0
IGT (cm/sn)	>116	>116	>116	>116	>116	>116
Thickness (mm)	0.67	0.65	0.66	0.67	0.67	0.68

Table 13. Physical and Optical Properties of Glossed Sample 2 Calcite Coated Papers by Using 12 % Latex.

Calcite ratio (%)	30	40	50	60	70	100
Humidity (%)	4.6	4.7	5.1	4.8	5.0	4.9
Brightness (Elrepho R-457, %)	86.3	86.6	86.7	86.9	87.2	87.8
Yellowness (Elrepho R-457, %)	-1.4	-1.6	-1.7	-2.2	-2.6	-3.4
Gloss (fotovolt 75°C)	81.7	80.1	76.0	72.0	68.0	65.5
IGT (cm/sn)	>116	>116	>116	>116	>116	>116
Thickness (mm)	0.65-0.67	0.65	0.66	0.66	0.67	0.68

Table 14. Physical and Optical Properties of Glossed Sample 2 Calcite Coated Papers by Using 13% Latex.

Calcite ratio (%)	30	40	50	60	70	100
Humidity (%)	4.6	5.0	4.8	5.1	4.9	4.7
Brightness (Elrepho R-457)	85.9	86.1	86.4	86.8	87.0	87.5
Yellowness (Elrepho R-457)	-1.3	-1.5	-1.6	-1.9	-2.2	-2.8
Gloss (fotovolt 75°C)	82.6	82.2	78.1	74.5	69.3	67.1
IGT (cm/sn)	>116	>116	>116	>116	>116	>116
Thickness (mm)	0.66	0.65	0.65	0.66	0.68	0.66

In the same manner, yellowness values are decreased with the decrease of glossing of sample 2. Whereas, brightness values are slightly increased with the decrease of glossing of sample 2 (Tables 6, 7, 8 and 12, 13, 14).

4. RESULTS AND SUGGESTIONS

As a result of the evaluation of the data obtained it is concluded that the percentages of fraction under 2 micron particle size and over 10 micron particle size have been within required limits for samples 1 and 2. The results obtained can be summarized as follows:

1. Brightness value decreases with higher latex rates and increases with higher calcite ratio.
2. Yellowness increases with the increase of calcite ratio and decreases with higher latex ratio.
3. Denisson wax values increase with the increase of latex ratio.
4. Cobb size values have been within required limits.
5. Gloss values have been much more than minimum value. Gloss value have been increased with higher kaolin and latex rates, but decreased with higher calcite rate.
6. Glossing has a beneficial effect on yellowness and brightness.
7. IGT test values are over the minimum value.
8. When using kaolin-calcite mixture for coating formulation optimum calcite ratio was found as 55%-65%.
9. Utilization of domestic calcite as coating pigment will provide foreign currencies saving. Consequently, two samples have been classified as high quality coating calcite.

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