CEC and its application in off-the-road tires

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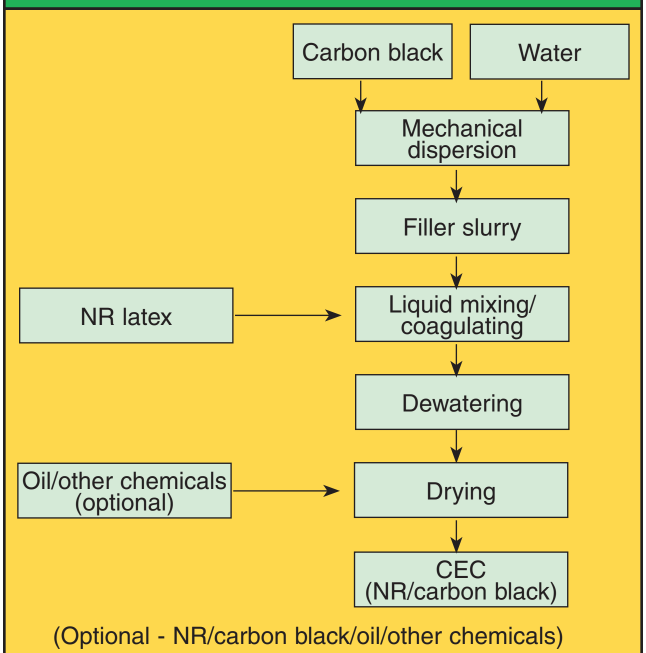
Cabot elastomer composites (CEC) materials are carbon black filled natural rubber masterbatches. Unlike any traditional masterbatch production, Cabot has developed a novel technology which continuously disperses carbon black in clean natural rubber latex (refs. 1-3). CEC material, produced by this continuous process, has the following features:

- Carbon black highly dispersed in rubber matrix;
- high bound rubber content;
- high rubber molecular weight; and
- no contamination from possible foreign materials such as dirt, leaves, sand, pieces of wood and wire.

These features bring improved performance to the products made of CEC material (refs. 4 and 5). In addition, rubber compounding process and materials handling can also be simplified, leading to enhanced productivity with the existing facility capacity.

In this article, we report the work on the application of CEC material to off-the-road tires. On each 18.00-25 tire, two-section treads were made with CEC material as one section and the corresponding dry mixed compound as the other section. Two formulations, 100% natural rubber formulation and natural rubber/synthetic rubber blend formulation, were used. In the blend formulation, CEC material was blended with synthetic rubber masterbatch. Mixing processes were carried out in plant scale mixers such as XM-140 and PN370. Compound properties, OTR tread wear and tread cut-and-chip results are presented.

Figure 1 - CEC process



CEC production process

The process of CEC production (figure 1) consists of carbon black slurry make-up, NR latex storage, mixing and coagulation of carbon black slurry and latex, dewatering of the coagulum, drying, finishing and packaging.

The carbon black slurry is prepared by finely dispersing carbon black in water mechanically without any surfactant. The slurry is injected into the mixer at very high speed and mixes continuously with the NR latex stream. Under highly energetic and turbulent conditions, the mixing and coagulation of polymer with filler is completed mechanically at room temperature in less than 0.1 second, without the aid of chemicals.

After dewatering of the coagulum in an extruder, the material is continuously fed into the dryer to further reduce the moisture to less than 1%. The residence time in the dryer is 30-60 seconds. Over the entire drying process, only for a very short period, typically 5-10 seconds, will the compound temperature reach 140-150°C. This is to say that during drying, the thermo-oxidative degradation of natural rubber can be essentially prevented. In the dryer, small amounts of antioxidants are also introduced as a stabilizer for storage. Optionally, the small ingredients in the compounds, such as zinc oxide, stearic acid, antiozonants, antioxidants and wax can be added in this stage.

The dried material can then be slabbed, cut or pelletized. Currently, CEC material is packaged into highly friable bales consisting of compressed small strips.

The key feature of the CEC process is the fast mixing and coagulation, and a short drying time at high temperature. This ensures excellent performance for the material as polymer-filler interaction can be better preserved and polymer degradation can be nearly eliminated.

Internal mixer mixing process

For an internal mixer, the difference between conventional mixing and CEC mixing is that in the conventional process, the mixer is loaded with low viscosity rubber and free flow filler. In mixing CEC material, an internal mixer is loaded with carbon-black-filled-masterbatch which may have a high viscosity, depending on the type and the loading of carbon black and the loading of other additives (table 1). The challenge in mixing CEC material is to set up appropriate mixing parameters and operation procedures. When mixing CEC material which has a high viscosity, control of the initial

Table 1 - viscosity of some CEC grades

CB grade and loading Grade/phr	*Storage viscosity ML(1+4)@100°C*
N134/50	185
N134/45	167
N234/50	170
N234/45	153
N220/50	174

torque and the rate of increase in compound temperature are key issues in obtaining an effectively mixed CEC compound.

We have done CEC material mixing on an XM-140 mixer which has a batch size of 160 kg, a BP270 mixer which has a batch size of 200 kg and a PN370 mixer which has a batch size of 310 kg. We found that by using a smaller sized mixer, we could adapt a conventional mixing procedure to CEC mixing with minor changes in operating procedures, but in using larger sized mixers, we had to adjust mixing parameters such as rotor speed.

To achieve effective mixing with high viscosity CEC material, masticating the CEC masterbatch for a short period of time in the beginning of the mixing cycle is essential, because the effective mechanical breakdown of the compound happens at low compound temperature. A great deal of heat is quickly generated during compound mastication. As rubber is a poor heat conductor, heat removal or heat control is a critical parameter for CEC mastication efficiency. Heat removal by cooling is based on the contact area between the compound and the cooling surface of the mixer. A smaller mixer, which has a relatively high ratio of metal surface area to compound volume, is better in controlling compound temperature than a larger mixer, and hence is relatively straightforward to use the parameters set for conventional mixing. For a larger mixer, however, we adjusted mixing parameters to get a balanced rate in compound mastication and compound temperature.

XM-140 mixing

As described in table 2, CEC mixing was first carried out under the same conditions and formulations as in conventional dry mixing (CEC 1 and CEC 2). A current meter was used to guide the batch dumping point. We observed that CEC material was mixed in a shorter time than the dry mix compound (12.5’ vs. 14’), and that the mixed CEC compound showed a lower Mooney viscosity than the conventional mixed compound (74 vs. 98). During the mixing, a brief period of batch slippage occurred after the addition of a processing aid to both CEC compound and the dry mix compound. For the dry mix compound, the processing aid provided the required compound processability after two mixing stages. For CEC compound, since a low viscosity could be quickly achieved in this scale of mixing, the processing aid was not necessary. Therefore, we made two CEC compounds without the processing aid (CEC 3 and CEC 4), and they showed a further saving of two minutes of mixing time with similar compound viscosity to the conventional mixed compounds.

In CEC 3 mixing, without adding the processing aid, CEC compound only used 75% of the conventional mixing time and gave a comparable Mooney viscosity. This means that, in a 25% shorter time, CEC compound without a processing aid provided the same compound processability as the conventional compound with a processing aid.

PN370 mixing

Under the same mixing conditions as used for the conventional dry mix compound, CEC compound showed a very rough surface after sheeting out from a sheet-preforming machine. The batch was dumped based on the mixing time set for the conventional dry mix and compound temperature, but it looked like the batch was inadequately mixed.

The rough surface of the compound could be looked at as many hard gels mixed in the smooth matrix. We believe that part of the CEC compound was in low viscosity while part of it remained in high viscosity. As we have mentioned, the non-uniform mix was related to the rapid increase in the compound temperature under shear force, the poor heat conductivity of rubber, the distribution effect of rotors and the flow pattern of the compound in the mixer. Under high shear rate, a high viscosity compound would experience high shear force, which is then converted to heat that raises the compound temperature and reduces compound viscosity. To let each part of the batch experience the same amount of shear force requires time. So in the early stages of mixing a batch, the compound viscosity is variable within the batch. If the variation is too large, due to the fast increase of local compound temperature, the batch could be composed of hard islands within softer oceans. Since the islands were trapped inside the ocean (lower viscosity parts of the compound), the shear force could not effectively work on those higher viscosity parts of the compound. By the time the batch was dumped, a consistent viscosity batch had not been achieved, so the compound still looked nervy. While we were working on adjusting mixing parameters and mixing procedure to obtain a smooth appearance of CEC, however, we found that the nervy appearance of the first mixing stage CEC compound became very smooth after the second mixing stage. This phenomenon was never seen for conventional mixed compounds.

It was readily apparent that the common experience in conventional mixing could not been applied

Table 2 - XM-140 mixing conditions and results

Formulations	*CEC 1*	*CEC 2*	*Conventional mix 1*	*CEC 3*	*CEC 4*
CEC	150	90	-	150	90
Synthetic blend		60			60
NR	-	-	100	-	-
Carbon black	-	-	50	-	-
Processing aid	8	8	8	-	-
Other ingredients	15	15	15	15	15
Mixing condition					
Mixing procedures: rotor speed 20 rpm, ram pressure 5.0 kg/cm^2, 160 kg					
Add CEC	0”	-	-	0”	-
Add CEC and synthetic MB	-	0”	-	-	0”
Add masticated NR	-	-	0”	-	-
Add 2/3 of carbon black	-	-	2’	-	-
Add rest of carbon black	-	-	4’	-	-
Add additive 1	3’	4’	4’	4’	4’
Add additive 2	5’	6’	6’	5.5’	5.5’
Add processing aid	8.5’	10’	9.5’	-	-
Dump (min.)	12.5’	14’	14’	10.5’	11’
Dump temperature, °C	135	135	145	155	160
Compound viscosity					
ML(1+4)@100°C	73.6	72.9	97.5	95.5	94.6

exactly to CEC mixing. To overcome the inconsistent viscosity of CEC compound in the first stage of mixing, we controlled the amount of shear force by reducing the rotor speed and hence the compound temperature during mastication. The speed of the rotor was lowered at the beginning of the CEC mixing cycle and then raised up after the addition of the small chemicals. The procedure that we set up after a few trials required the same mixing time as used for a conventional dry mix, but no processing aid was used for the CEC material and the CEC compound was lower in viscosity than the conventional compound (table 3). On the sheet-preforming machine, the batch appeared as smooth as previous mixes on a smaller scale.

Blending CEC with other polymers

In blend formulations, CEC material is required to blend uniformly with other polymers. In the plant scale mixer, we blended CEC with either a synthetic rubber masterbatch or pure polymer and free carbon black.

• Blending CEC material with a synthetic rubber masterbatch can be carried out by using two masterbatches with the same carbon black loading or using two masterbatches with different carbon black loading. Since the carbon black has already been dispersed and distributed in each masterbatch, the migration of carbon black from one polymer matrix into another polymer matrix is greatly constrained. In this way, carbon black loading in two rubber phases can be manipulated to a certain level.

A synthetic rubber masterbatch with the same carbon black loading as CEC material was prepared using a conventional dry mix cycle. To obtain a blend with small domain morphology, we loaded the two masterbatches into an XM-140 mixer first and mixed them for a short period of time before adding other ingredients into the blend.

• Blending CEC material with pure polymer and free carbon blackcan be done. In most industry plants, pursuing maximum production rate leads to the need to simplify mixing processes. Blend mixing can be done in the same way as single rubber compound mixing. So, mixing CEC material with another polymer and free carbon black can be a practical process.

In a PN370 mixer, CEC material and other rubbers were loaded and mixed for a short period of time before fillers were added. Since the carbon black dispersion obtained with CEC material is so much better than that with conventional dry mix, the carbon black dispersion in such a prepared blend is naturally inferior to the pure CEC material.

Final mixing

Special modification of mixing procedures was only needed for the first stage of CEC mixing. For the final stage, CEC compound behaved the same as the conventional mix. In this experiment, all mixes containing CEC material were performed in two stages. For the conventional dry mix, there were three stages, including the natural rubber mastication stage, masterbatch stage and final stage.

Compound properties

Table 4 lists the properties and performance of CEC material in two OTR tread formulations and the correspondent conventional dry mixed compounds.

Uncured compound properties

In the natural rubber formulation, CEC compound showed a slightly lower Mooney viscosity and a higher bound rubber content than the correspondent conventional dry mix. CEC compound usually possesses a higher bound rubber content due to its excellent carbon black dispersion. The achieved compound viscosity guaranteed smooth processing during extrusion. In the blend formulation, CEC compound showed a higher Mooney viscosity and a higher bound rubber content. Since two masterbatches were used in this CEC blend, while pure rubbers and free carbon black were used in the conventional dry mixed blend, the distribution of carbon black in the two rubber phases may not be the same for the CEC blend and the conventional blend. The higher viscosity of the CEC blend still produced an acceptable level of extrusion quality, however.

TEM micro-dispersion analysis of the CEC compound (CEC 5) and the dry mix compound (conventional mix 2) can be seen in figure 2. Clearly, the dispersion of the filler in CEC compound is considerably improved over the dry mix compound. In fact, as can

Table 3 - PN370 mixing conditions and results

Formulations	*CEC 5*	*Conventional mix 2*	*CEC 6*	*Conventional mix 3*
CEC	150	-	90	-
NR	-	100	-	60
Synthetic blend	-	-	40	40
Carbon black	-	50	20	50
Processing aid	-	8	-	8
Other ingredients	15	15	15	15
Mixing condition				
Rotor speed, rpm	30 then 40	40	30 then 40	40
Ram pressure, kg/cm^2				
Fill factor	0.75	0.75	0.75	0.75
Mixing procedures				
Add CEC	0”	-	-	-
Add CEC and synthetic rubber	-	-	0”	-
Add masticated NR and synthetic rubber	-	0”	-	0”
Add all fillers	-	0”	60”	0”
Add all additives	40”	0”	60”	0”
Add processing aid	-	at 125°C	-	at 125°C
Dump (min.)	at 150°C	at 150°C	at 150°C	at 150°C
Compound viscosity				
ML(1+4)@100°C	97.7	103.2	110.5	109.4

be seen in figure 2, carbon black dispersion and distribution in CEC compound was already complete in the CEC production process, as shown by CEC bale.

Curing characteristics

Generally, CEC compound showed the same curing characteristics as the conventionally dry mixed compound.

Physical properties

There wasn't a significant difference in physical properties between the CEC vulcanizate and the conventional dry mixed vulcanizate. Due to the better carbon black dispersion and the low level of compound defects, CEC vulcanizate usually showed slightly higher tensile than the correspondent conventional compounds. In the case of pure CEC applications, CEC vulcanizate often showed a lower hardness than the correspondent conventional dry mix. This is also attributed to the better carbon black dispersion in CEC material.

Dynamic properties

CEC vulcanizate showed higher rebound and lower hysteresis than the correspondent conventional dry mix. In figure 3, we can see that CEC vulcanizate had a lower Payne effect than the conventional dry mix, which substantiates the excellent carbon black micro-dispersion in CEC material. For blend compounds, it was found (ref. 6) that their dynamic properties are related to how they are prepared. In this work, CEC 4 was blended in a different way from the conventional dry blend. The vulcanizates showed similar dynamic properties.

Tearing and cut-and-chip

CEC vulcanizate showed higher tear strength than the conventional dry mix. The natural rubber compounds had better tear strength than the NR/synthetic rubber blends. This is also reflected in the cut-and-chip testing result where the loss percentage in the wheel diameter was larger for the blends than for the NR compounds. But in both NR and blend formulations, CEC vulcanizates changed less than the conventional dry mix.

Fatigue

Fatigue characteristics were measured by two tests, including crack growth rate which was described in a previous work (ref. 4) and fatigued physical properties.

CEC vulcanizates showed a lower crack growth rate than the correspondent conventional dry mix and similar fatigued physical properties to the conventional dry mix.

Abrasion

Abrasion tests were carried out on both a Cabot Abrader and a DIN Abrader. On both machines, CEC vulcanizates showed higher abrasion resistance than the conventional dry mix. Blended compounds were better than the NR compounds in abrasion resistance.

Tire building and road test

The best test of a new material is in its real world application. However, experience tells us that

Table 4 - compound properties and performance

	CEC 3		Conventional mix 1		CEC 3		Conventional mix 3	
Formulations								
CEC	150		-		90		-	
Synthetic blend	-		-		60		-	
NR	-		100		-		60	
Synthetic rubber	-		-		-		40	
Carbon black	-		50		-		50	
Processing aid	-		8		-		8	
Other ingredients	15		15		15		15	
Bound rubber, %	60		52		44		36	
ML(1+4)@100°C, final stage	76.6		78		80		73	
ML, dN.m (150°C)	7		8		7.9		7.9	
MH, dN.m	31.3		30.3		34.2		33.5	
T10	14.9		13.7		16.1		14.9	
T90	35.9		30.0		40.9		40.2	
Scorch time (120°C)	>60'		60'5"		>60'		57'14"	
Curing time, 137°C x min.	40'	80'	40'	80'	40'	80'	40'	80'
Tensile, MPa	27.8	26.8	25.2	25.5	23.1	25.6	23.8	22.8
Elongation, %	560	555	585	490	570	535	590	515
M300, MPa	13.8	13.3	11.8	12	10.8	13.4	10.6	11.7
Permanent set, %	26	25	29	23	23	18	26	17
Hardness	69	69	72	72	68	71	67	69
Tear strength, (KN/m)	162	152	145	141	129	140	136	106
Akron abrasion, cm^3/1.61 km		0.22		0.30		0.13		0.16
After 100K cycle fatigue								
Tensile, MPa		25.4		24.5		22.8		22.2
Elongation, %		520		530		480		480
Fatigue coefficient		0.89		0.86		0.80		0.91
80' sample, aged @ 100°C x h	24	72	24	72	24	72	24	72
Tensile, MPa	24.6	21.1	23.3	18.2	22.6	18	21.4	17.5
Elongation, %	465	405	490	385	420	385	420	350
Tear strength, (KN/m)	137	111	121	82	90	70	104	94
Aging coefficient	0.77	0.57	0.76	0.46	0.69	0.45	0.77	0.52
Akron abrasion, cm^3/1.61km	0.24		0.37		0.14		0.18	
Curing temp. 150°C								
Rebound, %, r.t.	47.3		39.7		42.5		41.3	
Rebound, %, 60°C	56.2		48.1		49.6		49.6	
Tan δ_{max}@60°C, 10Hz	0.188		0.238		0.209		0.211	
Cut and chip, diameter loss, %	8.3		9.1		9.9		10.3	
Crack growth rate								
(x10e-6), cm/million cycle	3.59		4.76		3.41		3.76	
Cabot abrader index, 7% slip	120		107		146		116	
Cabot abrader index, 14% slip	109		106		110		83	

real world field tests have more chaos than a lab test, so even with a single formulation, a high variation can be obtained in the results. To minimize the known variables during the road test, such as different trucks, more than one driver and at least six tire positions in a truck, we decided to build each tire with two tread sections, i.e., half of the tread used the conventional dry mix and the other half used CEC material.

The size of the OTR tires was 18.00-25 (figure 4). Section A was compared with section B in one tire, and section C was compared with section D in one tire. Section A was made with 100% CEC compound, and section B was made with 100% NR conventional dry mix. Section C was the blend made of 60% CEC material and 40% conventional synthetic rubber blend, and section D was the blend made by the conventional dry mix of 60% NR and 40% synthetic rubber blend.

The tires were equipped on 50-ton trucks which run on the field of an open mine in the center of China.

Figure 3 - strain sweep of CEC 3 and conventional compound 1 at 60°C, 10 Hz

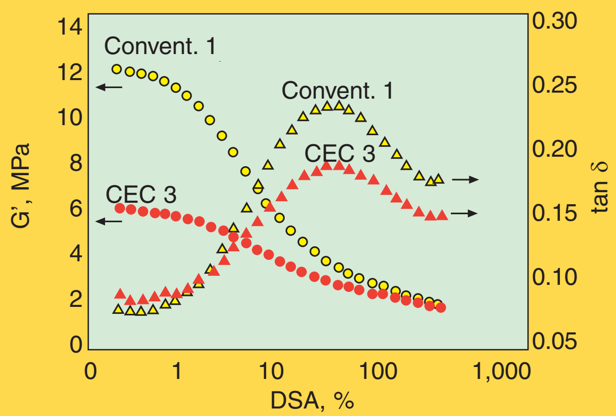
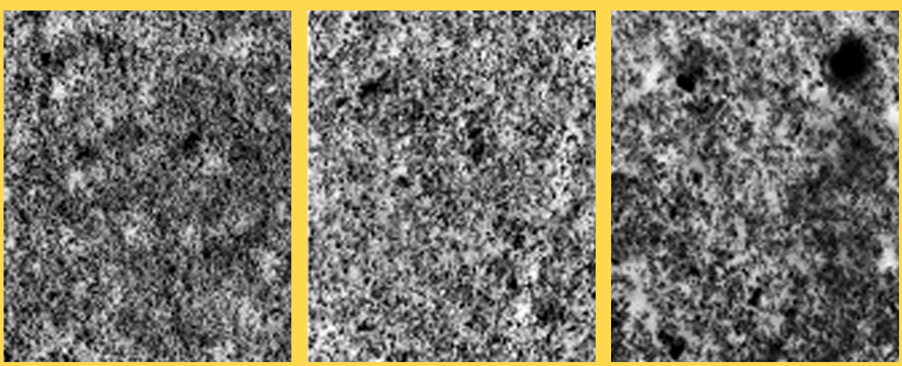


Figure 4 - two section road test tires

Road test results and discussion

The tires were run on very rough roads with heavy loads. On several tires, sharp rocks cut through the tread, and the tires had to be removed from the truck to be repaired. Cutting and chipping along the tire shoulders was evident at all times. However, the overall service life of the tire depended mainly on the wear of the tread. By measuring the remaining tread thickness of the tire at a fixed distance from one shoulder, at the end of their service life, we obtained comparable data on the material wear resistance. Figure 5 shows photos of the treads of four materials after their service life. As can be seen, the treads of the conventional dry mix sections (i.e., B and D) were worn through in the center and this made getting a representative measurement nearly impossible. We measured the tread wherever it could be found on the tire and used that to represent the remaining thickness of the conventional tread. For the two CEC sections (A and C), treads were left intact with a certain thickness. It was therefore obvious that if the tread were made with only CEC compound, the tire life would be longer. We used the above measurement technique to determine the average wear indexes from 22 tires. These are calculated and listed in table 5. Taking CEC counterparts as the reference, we can see that CEC material improved wear resistance at least 16% in the NR formulation and 12% in the blend formulation. Given that the CEC tread sections remained fully intact, it is evident that these wear resistance indexes are highly conservative, and that actual tire service life using the CEC material would have been longer.

Figure 2 - TEM micro-dispersion analysis of CEC bale, final mixed CEC compound and final dry mixed compounds



CEC bale — CEC final compound (CEC 5) — Conventional mix 2

We also compared the cut-and-chip performance of the two formulations and four compounds by counting the size and number of chipped patterns. To quantify the cut-and-chip performance, we classified the chips based on their size and used the whole pattern as one unit. If a whole unit of pattern was chipped, we took it as one chip at a size equal to "1 pattern." If a half unit of pattern was chipped, we took it as one chip at a size equal to "1/2 pattern." We counted the number of 1 pattern, 1/2 pattern and 1/4 pattern along the two shoulders of each section of each tire. These were averaged across the total number of tires

Figure 5 - comparing of treads after road test (A - CEC; B- conventionally mixed rubber; C - CEC blend compound; D - conventionally mixed blend compound

and then normalized the 1 pattern and 1/2 pattern to 1/4 pattern. From table 6 we can see that the NR compounds were better than the blend compounds in cut-and-chip resistance, and CEC compounds were better than the correspondent conventional compounds.

Conclusion

CEC materials have shown at least 12% to 16% improvement in the tread life in an OTR tire application, used in a NR/synthetic rubber blend formulation and in a 100% natural rubber formulation. With CEC material, the OTR tire plant was able to eliminate the natural rubber mastication stage from the tire process and, in total, save mixing time by at least 30%. Better performance, a simplified process and higher productivity have been achieved by using CEC materials.

Table 5 - wear resistance of treads after road test

Tread section	*Compound type*	*Average service life (day)*	*Tread initial (mm)*	*Average tread remained (mm)*	*Tread wear (mm/day)*	*Wear index*
A	CEC 3	122.7	38	10.1	0.227	116
B	Convent. 1	122.7	38	5.68	0.263	100
C	CEC 4	132	38	11.2	0.203	112
D	Convent. 3	132	38	7.95	0.228	100

Table 6 - cut-and-chip resistance of treads after road test

Tread section	*Compound type*	*Average service life (day)*	*Average pattern chipped at shoulder*			*Normalized*
			1 (unit)	*1/2 (unit)*	*1/4 (unit)*	*1/4 (unit)*
A	CEC 3	122.7	0.2	1.3	1.6	5
B	Convent. 1	122.7	0.2	1.4	1.4	5.2
C	CEC 4	132	0.8	1.2	5.4	11.0
D	Convent. 3	132	1.4	2.0	4.2	13.8

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