

# GAS EVOLUTION FROM RESIN-BONDED SAND CORES PREPARED BY VARIOUS PROCESSES

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## Abstract

The present work is focused on the measurement of the rate and amount of gases evolved from various cores for aluminium casting. Specimens were selected from normal production at Carmagnola Plant of Teksid Aluminium, including furanic hot-box cores, phenolic shell-molding cores and phenolic isocyanate-urethane cold-box cores with different percentages of resins. The results show that the volume of gas evolution increased with temperatures and the rate of gas evolution, for any categories of cores, was more remarkable at higher temperature. A light increase of resin contents in cold-box cores caused a much higher increase of gas evolution. Moreover, furanic hot-box cores showed an early and rapid evolution and reached their peak evolution earlier than cold-box ones. The data obtained from this study can be used to explain the gas-related problems for aluminium casting and, as references, to modify the resin contents and the proportion of different resins in normal production.

## Riassunto

Questo lavoro tratta della misura della quantità e velocità di emissione del gas sviluppato dai diversi tipi di anime usate nelle fonderie di alluminio. I campioni sono stati selezionati dalla normale produzione nello stabilimento della Teksid Alluminio a Carmagnola. Includono delle anime furanic hot box, delle anime phenolic shell-moulding e delle anime phenolic-isocyanate urethane, con delle percentuali di resine diverse. I risultati dimostrano che sia il volume di gas sviluppato che la velocità di emissione è aumentato con la temperatura, per ogni tipo di anima. Un aumento leggero della percentuale di resina per anime cold-box coinvolge un'emissione di gas molto più alta. Inoltre le anime furanic hot box dimostravano un incremento di gas precoce e rapido e raggiungevano il colmo della loro emissione più presto delle anime cold box. I dati ottenuti da questo studio possono essere usati per spiegare i problemi collegati al gas nelle colate di alluminio, per modificare le percentuali di resina e le proporzioni delle diverse resine nella produzione normale.

## INTRODUCTION

The rate and amount of gas that is evolved from a resin-bonded sand during the aluminium casting operation is one of the most important properties of the cores. The numerous different binder systems in use all have different responses to the heat of the casting process, and produce gases of different kinds, in different amounts, at different times, and at different rates. It will be very useful to understand the behaviours relative to gas evolution of the cores prepared by different processes and with different binder systems in our normal production.

Although a new binder system – the GMBOND™ core making process – is proved at Teksid for safety aluminium suspension parts [1, 2], several commercial and traditional core making processes are still being in use for principal normal production of cylinder heads and blocks. These processes include furanic hot-box process, phenolic isocyanate-urethane cold-box process and phenolic shell-moulding processes. All of them show excellent performance for core production rate, core strength and surface finish,

core dimensional accuracy and stability.

To measure the gas evolution of the cores prepared by these processes is useful not only for explaining the environmental problems (exhaust fumes) but also for understanding the problems in production such as gas-related defects in casting and residue build-up in mould. In particular for the production of cores with complicated shapes and thin parts, higher content of resins has to be used to guarantee core strength. In this case the deposition from the burned resin in mould becomes serious which will have influence on normal production and sometimes causes defects to castings.

It is very difficult to find a method to determine the rate and amount of the gas evolved from cores which corresponds with any accuracy to the

conditions of casting. Difference between laboratory test and real production may be resulted from many factors such as the temperature(test temperature in laboratory may be not the same of real casting operation), the

percentage of resin burnt in cores, the physical characters of cores (density, porosity, humidity) etc. However if we use the same test instrument, laboratory test can help us to compare the gas evolution level among different cores produced by various processes (different resin either for categories or for content).

TEST MACHINE AND  
GENERAL PRINCIPLES

The machine used to test gas evolution in our laboratory is Gas Determinator 306, product of Ridsdale & Co. Ltd.  
This method of determining the gas content of sands depends upon the introduction of a weighted

sample into a heated tube filled with an inert gas and measurement of the increase in pressure due to the gas evolved from the sample.  
Pressure readings are converted to volumes by means of a calibration graph prepared at the operating temperature.  
The tube is heated in a furnace with an inclined heating chamber which ensures that the evolved gases remain in the hot zone and only the inert passes into the pressure recorder[3].

EXPERIMENTAL PART

CALIBRATION

A pressure-volume graph is prepared as follows: weigh increments of potassium hydrogen carbonate ( $\text{KHCO}_3$ ), previously dried for 30 minutes at  $105^\circ\text{C}$ , into copper sample tubes and plug with BDH Triton Kaowool. Inject these specimen tubes into the furnace and record the maximum pressure attained. Plot maximum pressure against theoretical volume of gas evolved at N.T.P., i.e. 224ml per gramme of dry  $\text{KHCO}_3$ , [4]

Wt. Of $\text{KHCO}_3$	Theoretical Vol. At N.T.P.
0.05g	11.2ml
0.10g	22.4ml
0.15g	33.6ml
0.20g	44.8ml

One example of the calibration results is plotted in Fig. 1.

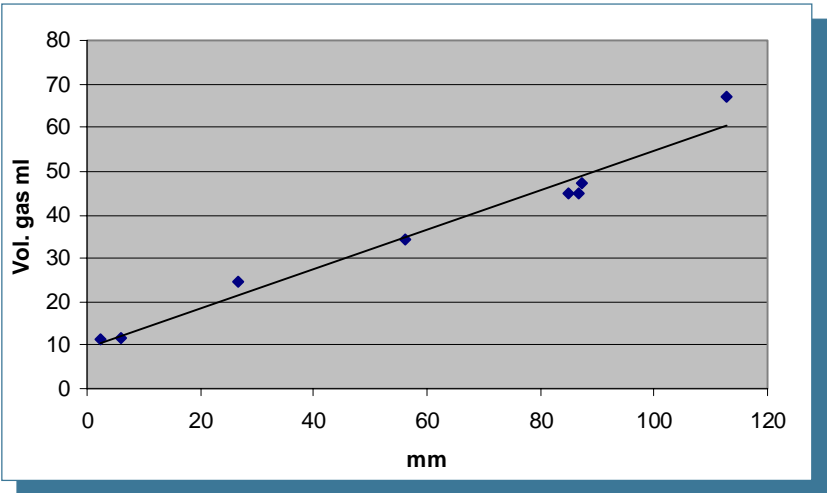


Fig. 1: Calibration of pressure/volume gas

TEST PROCEDURE

Specimens are sand cores of normal production at Carmagnola Plant of Teksid Aluminium, including furanic hot-box cores, phenolic shell-moulding cores and phenolic isocyanate-urethane cold-box cores with different percentages of resins.  
The test procedures are described in detail in the instructions of the instrument[4]. Several important steps are summarized as below. Set the

temperature controller to the required temperature (e.g.  $700^\circ\text{C}$  or  $850^\circ\text{C}$ ) and allow the furnace to attain equilibrium at this temperature. Introduce a weighed quantity (about 2g) of core (pulverized) into one of the special thin-walled copper sample tubes (75 mm long ´ 6 mm diameter, closed at one end) and plug the open end with BDH Triton Kaowool. Insert the sample tube into the spring-gun assembly with the gun in the “loaded” position. Make pass a stream of oxygen-free nitrogen through the apparatus and expel all oxygen (or gases from a previous test). Shut off the supply of nitrogen and wait for 2 minutes to allow the gas in the tube to attain furnace temperature. Switch on the recorder and inject the sample tube

TABLE 1. TESTS OF GAS EVOLVED FROM DIFFERENT CORES

Aim of Tests	Test conditions	Specimen*
Gas evolution vs temperature	200°C – 300°C – 400°C – 500°C – 600°C – 700°C – 850°C	<ul style="list-style-type: none"> <li>Furanic (1.4%) hot-box core</li> <li>Phenolic isocyanate-urethane cold-box core (1.2%: 0.6% phenolic and 0.6% isocyanate)</li> </ul>
Gas evolution vs Core category	850°C	<ul style="list-style-type: none"> <li>Furanic (1.4%) hot-box core</li> <li>Phenolic shell-molding core (2.2%)</li> <li>Phenolic isocyanate-urethane cold-box core (1.2%: 0.6% phenolic and 0.6% isocyanate)</li> <li>Phenolic isocyanate-urethane cold-box core (1.6%: 0.8% phenolic and 0.8% isocyanate)**</li> </ul>
Gas evolution vs time	700°C – 850°C up to maximum gas evolution	<ul style="list-style-type: none"> <li>Furanic (1.4%) hot-box core</li> <li>Phenolic shell-molding core (2.2%)</li> <li>Phenolic isocyanate-urethane cold-box core (1.3%: 0.65% phenolic and 0.65% isocyanate)**</li> </ul>

\* Resin content in each process is indicated in parentheses.

\*\* For a cold-box of making four different cores with complicated shapes and thin parts.

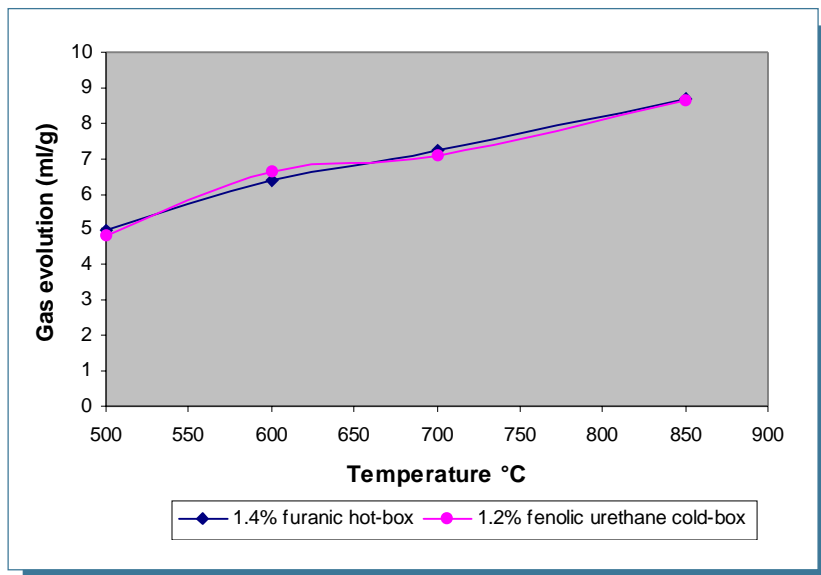
into the hot zone. Switch off the recorder as soon as the record pen stops rising.

The rate of gas evolution can be observed from the pressure curve traced out on the recorder.

The total volume of gas evolved (corrected to N.T.P.), or the volume of gas evolved after any period of time after injecting the sample into hot zone of the furnace, can be obtained by reference to the pressure/volume graph plotted in Fig. 1.

Tests were performed at 700°C and 850°C respectively for above-mentioned all three categories of cores. Mean value was obtained by 4

measurements for each condition of each category. For studying the relationship between gas evolution and temperature, tests were performed also at 200°C, 400°C, 500°C, 600°C up to 850°C respectively for furanic hot-box cores and phenolic urethane cold-box cores, two main core-making processes for our normal production. For simplicity, all the tests performed are reported in Table 1.



## RESULTS AND DISCUSSION

### 1 GAS EVOLUTION – TEMPERATURE

Furanic hot-box and phenolic isocyanate-urethane cold-box are two main core-making processes in use at Teksid Aluminium. Gas evolution from these two types of cores was tested at different temperature from 200°C to 850°C. The results shows that the gas evolution was unobservable for these specimens at temperatures until 400°C. The temperatures of auto-ignition of resins may account for this phenomenon. They are respectively approximate 400°C for furanic (hot-box) and phenolic (cold-box), 450°C for isocyanate (cold-box).

Fig. 2 shows the quantities of gas evolved from the two main cores at temperatures from 500°C to 850°C, which increase slightly with temperature.

Fig. 2: Gas evolution from furanic hot-box and phenolic urethane cold-box cores at different temperature

## GAS EVOLUTION – CORE CATEGORIES

The amount of the gas evolved from 1.2% phenolic isocyanate-urethane cold-box cores is similar with that from 1.4% furanic hot-box cores (Fig. 1). It should be noted that the content of binders (phenolic and isocyanic 1.2%) in cold-box is less than that used in hot-box (1.4% furanic). If we use a cold-box core with higher content of binders, we can suppose that the gas evolution should be increased. This is confirmed by the fact of using 1.6% binders (0.8% phenolic and 0.8% isocyanate) in cold-box cores with complicated shape and thin part (e.g. water jackets) to guarantee their mechanical strength. Fig. 3 gives the comparison of the gas evolved from various cores at 850°C. From the comparison of 1.2% and 1.6% phenolic isocyanate-urethane cold-box cores, it can be seen that increase only 0.4% binders yields a much higher evolution of gas (55% increased).

As we have seen, the phenolic urethane cold-box system is comprised of two resin parts. Part 1 is a phenolic resin dissolved in an organic solvent, and Part 2 is an isocyanate component dissolved in a similar solvent. For making cores for aluminium castings, the binder in this system typically is used at a level of about 1% of the sand weight. The Part 1:Part 2 ratio (by weight) is usually offset to 60:40 to improve shakeout, reduce cost and minimize gas-related defects[5]. The contents of binders are higher than 1% for the cores used in Teksid Carmagnola. The results of gas evolved from cores using different percentage of binder show that a light increase of binders (e.g. 1.2% – 1.3% – 1.6%) causes a much higher increase of gas evolution

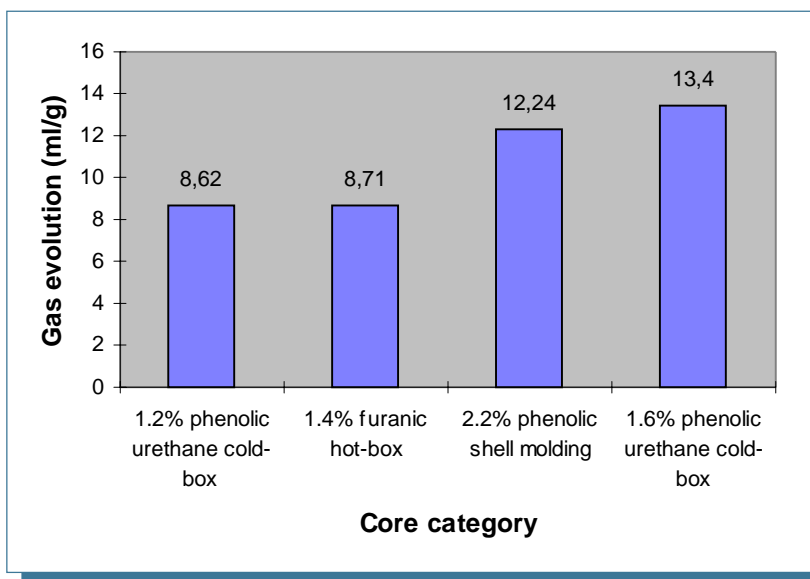


Fig. 3: Gas evolution of various cores at 850°C

(8.62 ml/g – 10.45 ml/g – 13.4 ml/g). Although at present the phenolic isocyanate-urethane systems are among the lowest overall producers of volatiles[6], the volume of gas evolved is, of course, proportional to the amount of binder present. In addition, the organic resins and solvents in the phenolic isocyanate-urethane system make it high in carbon content, which contributes to the formation of lustrous carbon and a reducing mould atmosphere during casting[7]. This may explain the reason of residue deposition on the mould when using cold-box cores with higher binder levels. From the instruction materials of resin providers, it seems that the Part 2 (isocyanate) will be useful to increase the strength of cold-box cores, but at the same time it may produce more gas. Many foundries use slightly more Part 1 for various technical reasons as indicated before.

As for the phenolic shell-moulding process, higher percentage of resin (2.2%) is used and causes higher gas evolution.

## GAS EVOLUTION – TIME

The gas evolution rate of various cores at 700°C and 850°C is shown in Fig. 4.

First of all we have noted the difference among curves obtained at different temperatures. For any category of cores, the volume of gas evolved at 850°C reaches its peak rate in a time much shorter than that at 700°C. It means that for the same binder, the rate of evolution of gas (the slope of the curves in Fig. 4) is different at different temperatures. At higher temperatures the gas should be evolved in a higher velocity.

For cores prepared by different processes with different binders, the phenolic shell-moulding cores started gas evolution later than other types of cores and then reached its peak rate in a great

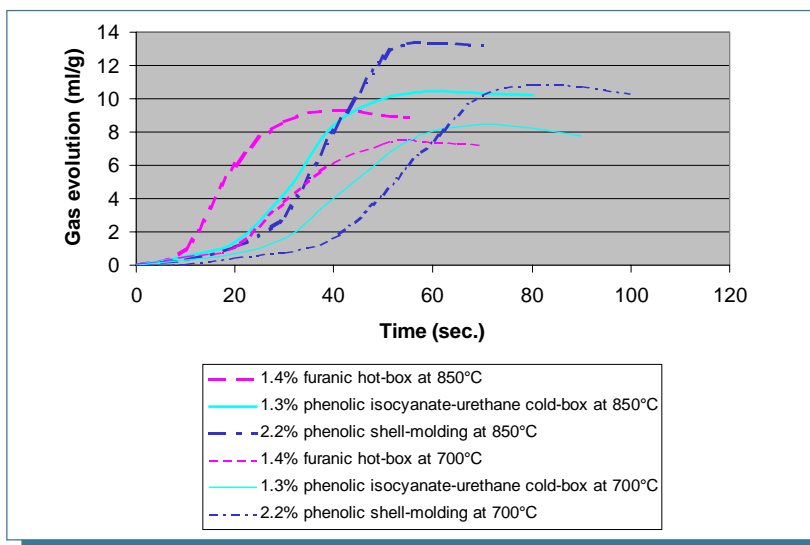


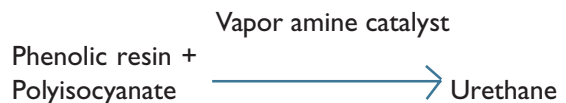
Fig. 4: Gas evolution rate of various cores

velocity because of the highest content of resin. However, since the shell-moulding process was used only for making intake ducts core in some cylinder head, it did not cause serious problem of deposition in mould like the cold-box cores which are used at complete package.

Comparing the curves of gas evolution from cold-box cores with those from hot-box cores we can see that, at the same temperature, furan hot-box core shows an early and rapid evolution whereas phenolic isocyanate-urethane core produces most of its gas about 10 seconds later than hot-box one. For instance, at 850°C, hot-box core shows sensible evolution of gas at the 10<sup>th</sup> second and reaches its maximum evolution at the 40<sup>th</sup> seconds, while cold-box core begins a sensible evolution at the 20<sup>th</sup> second and shows its peak evolution at the 60<sup>th</sup> second. At 700°C, the sensible evolution of gas for hot-box core began at the 20<sup>th</sup> second and its maximum was reached at the 55<sup>th</sup> second, while for cold-box core the sensible evolution was shown at the 30<sup>th</sup> second and the peak evolution at the 70<sup>th</sup> second. The difference behaviour between hot-box and cold-box cores can be explained from two aspects. On the one hand, the temperature of auto-ignition of furanic resin for hot-box process is lower than that of both phenolic and isocyanate for cold-box process. Therefore, hot-box core shows a sensible evolution of gas earlier. On the other hand, the different reaction mechanism during core-making between two processes may result in the different behaviour in gas evolution. A simplified hot-box reaction mechanism is:

Furanic liquid resin + Catalyst + Heat → Solid resin + Water + Heat

On the contrary, the urethane reaction during cold-box processing does not produce water or any other by-product. A simplified curing reaction mechanism for the phenolic urethane cold-box process is:



The most distinctive feature of the phenolic urethane amine system is the amine catalyst. There are two types of amines that are commonly used as the catalyst – triethylamine (TEA) and dimethylethylamine (DMEA). DMEA is the more effective catalyst, but, because of its stronger odor, higher cost and only marginal improvement in total machine cycle (with properly rigged tooling), most of the larger aluminium operations use TEA[5]. The boiling point of TEA is very high. It will be condensed in cores if the operating temperature is not enough and, in this case, will create more gas.

Moreover, as shown in Fig. 4, the peak evolution of gas from 1.3% phenolic isocyanate-urethane cold-box cores was higher than 1.4% furanic hot-box cores, despite the fact that the cold-box cores started the sensible evolution later. This may explain why the cylinder head mold where complete package cores were cold-box processed showed more serious gas-related problem such as tar residue.

## EXPERIMENTAL RESULTS AND SITUATION OF NORMAL PRODUCTION

As indicated at the beginning of this work, it is very difficult to find a method to determine the rate and amount of the gas evolved from cores which corresponds with any accuracy to the conditions of casting. Although the experimental results can be used to compare the gas evolution among various core-making processes, there will be differences in several aspects:

- With the test machine in this work, only about 2g cores are used for each test. In this case, resins in the specimen should be burnt completely (or almost 100%) at the test temperature within the given time at which the evolution of gas reaches its maximum value. While in the case of casting, only the superficial zone with a limited thickness of the core which is covered by liquid metal suffers from high temperature. The temperature decreases remarkably towards the central zone of the core because the silica sands are not a good thermal conductor. Therefore, the resins in the core cannot be completely burnt during the casting. The volume of gas evolved increases with the increase of the burnt percentage of resins in core for real casting.
- Temperature has strong influence on the rate and amount of gas

evolution. So the gas-related problems in casting operation depend also on the temperatures of the pouring metal as well as of the mould.

- In laboratory tests the specimens are in powders, the outgassing will be easier than in real casting operation where the cores are compacted in the given shape and covered by liquid metal.
  - The volume of gas evolved from cores in this work includes also gases originated from the moisture and other volatile substances. Before the test it is not introduced any predrying step.
- These experimental results are not to be taken as absolute in any sense. However, according to these data obtained in laboratory we can give a prediction on the rate and amount of gas evolution for various cores prepared by different processes or with different content of resins.

## CONCLUSIONS

The volume of gas evolved from various cores for our normal production – aluminium casting prepared by different processes has been tested using Gas Determinator. The gas evolution for hot-box cores, cold-box cores as well as shell-moulding cores were analysed in function of temperature, of time and so on.

The gas evolution was not observable before 500°C. The volume of gas evolution increases slightly with temperature from 500°C to 850°C. The amount of the gas evolved from 1.2% phenolic isocyanate-urethane cold-box cores was similar with that from 1.4% furanic hot-box cores at the same temperature. However, a light increase of

binders in cold-box process caused a much higher increase of gas evolution; the increase of only 0.4% of resins yields a much higher increase in evolution of gas as 55%.

The rate of gas evolution, for any category of cores, is more remarkable at higher temperature. As for the cores prepared by different processes, furanic hot-box cores show an early and rapid evolution and reach their peak evolution earlier than cold-box ones. The delays of cold-box cores are respectively 10 seconds for the starting of the sensible evolution and 20 seconds for reaching the peak evolution.

For the gas-related problems such as tar deposition in the mold where cold-box cores are used, our suggestion, at first, is to minimize the contents of resins and to modify the proportion of phenolic part and isocyanate part in guarantees of the mechanical strength of the cores. At the same time, we can seek for the way to facilitate the exits of gas through the modification of core structure and of the mould.

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## REFERENCES

1. Ferrero A., M. Badiali, R. Schreck, J.S. Siak and W. Whited. New binder for casting cores: an industrial application to safety suspension parts. International Congress and Exposition, Detroit, Michigan February 23-26, 1998. Product and Process integration: Advanced Technology (SP-1337) Paper n° 981005.
2. Mus C., M. Mattiel, D. Valzan, A. Delbianco and J. Tucker. Innovative foundry technologies for safety aluminum suspension parts and complex castings. SAE 2001 World Congress. Detroit, Michigan March 5-8, 2001. Automotive Casting processes and Materials (SP-1603) Paper n° 2001-01-0407.
3. Godding. B.C.I.R.A. Journal. 9 (1961), 687-692.
4. RIDSDALE & CO. LTD. Instructions RIDSDALE gas determinator. October, 1984.
5. Jorstad J.L. and W.M. Rasmussen. Chemically bonded sand molding and coremaking. In D.L. Zalensas (Ed.), Aluminum casting technology. American Foundrymen's Society, Inc., Des Plaines, Illinois, 1993, 2<sup>nd</sup> Edition, pp.203-221.
6. Campbell J.. Gas pressure in moulds and cores. In J.C. Worcester (Ed.), Castings. Butterworth Heinemann Ltd., Linacre House, Jordan Hill, Oxford OX2 8DP, 1995, pp.105-111.
7. Archibald J.J. and R.L. Smith. Resin binder processes. In ASM International Handbook Committee (Ed.), Metal Handbook 9<sup>th</sup> Edition, Metals park, Ohio, 1988, pp. 214-221.